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PROBABILITY EXPERIMENTALLY INVESTIGATED[1]

BY A. L. CLARK[2]

Abstract

This paper is the third and last of a series of papers on an experimental investigation on probability. Steel balls were dropped on a horizontal steel plate in which holes were bored in a regular pattern. The probability that a ball will pass through a hole without touching the plate is calculated from the known data and found to be 0.3554 ± 0.0005. The experimental value of the probability or the ratio of free passages to the total number of balls dropped is 0.35557. The agreement is very good. The numbers of runs of various lengths were calculated and compared with the actual numbers of these runs, again with good agreement. π may be calculated from the experimental value of the probability.

In two earlier papers (1, 2) the theory of an experimental study of probability and the apparatus used were described. The results of the observations up to 250,000 events were indicated and some conclusions were drawn. In the work described in this paper the number of observations has been increased to the half million mark.

Briefly, the experiment involves the dropping of steel balls on a horizontal steel plate pierced with circular holes arranged in a regular hexagonal (triangular) pattern. The observer records whether or not each ball passed through a hole without contact with the plate. A microphone attached to the plate makes detection of a contact easy.

The probability that a ball will pass through without contact is

$$P = \frac{2\pi(R - r)^2}{d^2\sqrt{3}} , \qquad (1)$$

where R and r are the radii of the holes and balls respectively, and d is the distance between the centres of adjacent holes. Substituting the measurements of these quantities in Equation (1) and making the correction for departure of the paths from the vertical (1) the calculated probability is

$$P = 0.3554 \pm 0.0005 .$$

Of the 500,000 balls dropped, 177,785 passed through freely which gives for the experimental value of the probability

$$P = 0.355568 .$$

[1] *Manuscript received June 2, 1937.*
Contribution from the Faculty of Applied Science, Queen's University, Kingston, Canada.

[2] *Dean of Applied Science, Queen's University.*

As will be seen, the agreement between the values of P is very close, better than the accuracy of the measurements of diameter and centre distances could be expected to give. Since the experimental value of P may be regarded as a very accurate approach to the true value of the probability, the close agreement between the experimental and calculated values of P indicates that the errors in measurements neutralize each other to some extent.

The value of P to date* oscillates erratically so that the value at the end of any series may not be the best value. The end of the series may show an abnormally high or low value depending on what has happened during the last part of the series. A process of interpolation (explained in the earlier papers) was employed to determine by judgment what would be the end value of an infinitely long series. This interpolated value is

$$P = 0.355570 ,$$

which is very close to the end value and is to be taken as the best value assignable from the data available. The last events of the series happen to run well in accord with theory.

Fluctuations

The fluctuations about the accepted value of P are shown in Table I, where the experimental values and the departures from the accepted value are shown for series lengths of 25,000, 50,000, and 100,000. Similar figures are shown for the values to date by 25,000's.

TABLE I

25,000		50,000		100,000		To date by 25,000's	
P	δ	P	δ	P	δ	P	δ
						.3546	−.0010
.35460	−.00097					.35496	+.0039
.35732	+.00175	.35596	+.00039			.35529	−.0028
.35396	−.00161					.35558	+.00001
.35644	+.00087	.35520	−.00037	.35558	+.00001	.35566	+.00009
.35596	+.00039					.35543	−.00014
.35428	−.00029	.35512	−.00045			.35586	+.00029
.35844	+.00287					.35550	−.00007
.35292	−.00265	.35568	+.00011	.35540	−.00017	.35552	−.00005
.35576	+.00019					.35555	−.00002
.35584	+.00027	.35580	+.00023			.35526	−.00031
.35236	−.00321					.355447	−.000123
.35348	−.00209	.35492	−.00065	.35538	−.00019	.355388	−.000182
.35448	−.00009					.355700	+.000130
.35976	+.00419	.35722	+.00165			.355555	−.000015
.35352	−.00205					.355640	+.00070
.35688	+.00131	.35520	−.00037	.35621	+.00064	.355591	+.000021
.35484	−.00073					.355567	+.000003
.35516	−.00041	.35500	−.00057			.355630	+.000060
.35668	+.00111					.355568	+.000002
.35448	−.00109	.35558	+.00001	.35529	−.00028		

* *The value "to date" is the value of P from the beginning of the series to any point where P is calculated.*

The percentage maximum fluctuations are shown in Table II.

TABLE II

Series length	Fluctuation, %	Series length	Fluctuation, %
100	18.0	25,000	0.42
1000	6.4	50,000	0.049
5000	1.8	100,000	0.011
10,000	1.42	250,000	0.0006

The rapid decrease in the value of the percentage maximum departure from the accepted value of P with the series length is significant. It is easy to see why the relative departure from equilibrium conditions is negligible when we are dealing with a very large number of events occurring with perfect randomness. For example, in the case of an appreciable volume of gas under moderate pressure the departure from the mean number of collisions of the molecules with the wall or with an object immersed in the gas is too small to be noticeable. When, however, the area of the wall or of the object becomes small enough then the number of events becomes small, and the relative fluctuations about the mean become large and effects become noticeable as with the Brownian movement.

The Value of π

In the first paper, the value of the probability was taken as 0.35556. This value when inserted in Equation (1) gives $\pi = 3.143$.

It must be remembered that the accuracy of the ratio of P to π is known only to five parts in 3500. Therefore, the value of π can legitimately be calculated only to the same accuracy. The value of P is now believed to be 0.355570. This value when substituted in Equation (1) gives

$$\pi = 3.145 .$$

If, however, we were to search the record of the observations we might, and probably would, find points in the series such that if we were to begin and end at these points and calculate the value of P, a very accurate value of π might result from substitution in Equation (1). For example, the value of P at the end of the series, stopping at 275,100 events, is 0.35525. This value when substituted in Equation (1) gives

$$\pi = 3.14167 .$$

No doubt a more favorable stopping point might be found. It is, however, not worth while to find such points as the value of π, deduced from the value of P, so found, would be misleading. The best value which can be assigned to π from this experiment is 3.145. This, while not very different from the previous value, is not quite as good. This means that the unavoidable inaccuracies in the measurements of R, r, and d are present in the calculation.

It is suspected that the remarkable determinations of P obtained by some observers from an experimental examination of Buffon's problem are not above suspicion.

Probability Curve

As before, the values of P by 100's were tabulated and the number of times each value of P appears in the table was plotted against P. The resulting

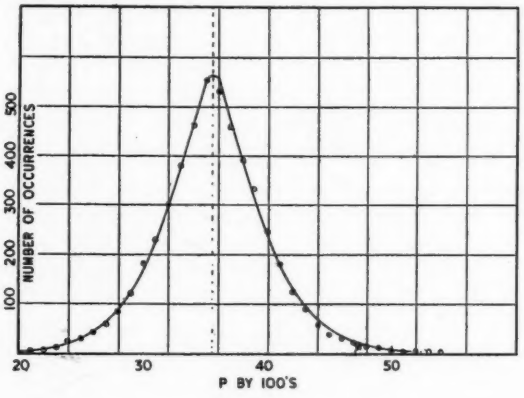


FIG. 1

curve is shown in Fig. 1 and is a very good picture of the ordinary probability curve. The points lie very well on the curve and it is very nearly symmetrical about the value $P = 0.3556$.

Sequences

When the number of events is large, the sequences or the continuous runs of favorable cases (free passages) may be calculated from

$$N = nP^k , \tag{2}$$

where k is the length of the run, N the number of times a run of length k appears, and n the total length of the series taken. The number of times each run actually occurred were counted and the results are shown in Table III. The columns in order show the sequence length, the calculated value of N, then the counted numbers of times the sequences appeared for series lengths of 100,000, and finally the calculated and observed values of N for the series 500,000.

Examination of the table shows clearly that the value of the experimental probability for a series length of 100,000 changes but little from series to series. Longer series produce even better agreement. The numbers of runs of 4, 5, 6, are not in very good agreement with theory. It must be kept in mind, however, that we are dealing, in the runs, with a relatively small number of events of the kind under discussion (runs) and the agreement may be disappointing. The fine agreement for shorter and longer runs must be regarded as fortuitous. The first 100,000 gave extraordinary agreement

TABLE III

Runs	100,000's observed						500,000	
	N, Calc.	1st	2nd	3rd	4th	5th	*N*, Calc.	*N*, Obs.
1	35557	35558	35540	35536	35461	35529	177785	177785
2	12643	12359	11532	12722	13283	12693	63215	62559
3	4496	4655	4195	5181	5378	5015	22477	24482
4	1598	1489	1223	1969	2088	1801	7992	8579
5	568	572	405	865	967	769	2841	3578
6	202	191	82	333	367	279	1010	1252
7	71	74	18	137	131	93	359	453
8	25	33	5	45	38	25	128	146
9	9	17	0	13	11	5	45	46
10	3	9	0	3	4	0	16	16
11	1	5	0	1	2	0	6	8
12	0.4	3	0	0	0	0	2.0	3
13	0.1	1	0	0	0	0	0.7	1

between observed and calculated values of *N*. The second series of 100,000 was very disappointing after the success with the first. It is to be expected, however, that while some series will show good agreement others will not.

The failure of the results to accord with those calculated from Equation (2) need not cast discredit on the formula, although it is always a question how reliable any formula for a probable value may be considered. Sometimes it is almost certain to fail to give what is expected. This is the nature of probability. In order to give a more adequate test a much longer total series must be taken.

It has been pointed out in this series of papers that while in a general way the results are entirely in accord with theory, there are many unexpected peculiarities. For example, and it is perhaps the most significant single result, a run of 13 appeared in the nineteenth thousand, whereas such a run should appear about once in a million trials. The often suggested waiting a long time for the improbable to happen may not be necessary and on the other hand, it may not appear, even in a run many times the length thought necessary—indeed it may not appear at all in a finite series. The practice so often employed in sampling of basing conclusions on relatively few observations may in some cases give results far from the truth. Generally speaking the larger the number of events in a series, the more assurance one may have that conclusions drawn from a study of this series are reliable.

Acknowledgments

The author wishes to thank Mr. E. Harris, Curator in the Department of Physics and a group of honor students in physics for carrying on the work of accumulating the data in this paper.

References

1. CLARK, A. L. Can. J. Research, 9 : 402-414. 1933.
2. CLARK, A. L. Can. J. Research, 11 : 658-664. 1934.

ABSORPTION STEP-WEAKENERS OF ANTIMONY[1]

By G. O. Langstroth[2] and D. R. McRae[2]

Abstract

It is of advantage to the spectroscopic analyst to have a means of quickly preparing a step-weakener of any required characteristics. A method has been developed in which antimony films are deposited by thermal decomposition of the trihydride. The apparatus required is simple, and a multi-step weakener may be made in 30 min. The films are nearly neutral below λ 4000Å. Their optical density is quite uniform, and they are sufficiently strong for all practical purposes. For high precision work, the construction of the weakener must be such that undesirable interference effects are avoided. A consideration of the theory of interference phenomena in light transmitted through thin plates suggests several possible methods of construction. Some of these have been adopted and have been found to be satisfactory in practice.

In quantitative spectroscopic analysis it is often desirable to photograph the spectrum of a sample in such a way as to obtain a series of graduated steps of known relative intensity with a single exposure. The photographic blackening of the spectral line in which one is interested will then lie in the "normal exposure region" for some particular step, and a precise measurement of it can be made. This procedure often results in a considerable saving of time and effort, and indeed may be a necessity in certain problems. Three common circumstances in which it is especially useful are: (1) when it is desired to analyze for several elements in each sample, (2) when the concentration of the investigated element varies widely from sample to sample, and (3) when results of the highest accuracy are not required. In the first, one exposure is sufficient for a complete analysis, whereas with the ordinary technique several exposures may be necessary, and these cannot be made if the sample is small. In the second, it is not necessary to take a trial plate for each sample in order to determine suitable conditions for exposure, as is the case with the ordinary technique. In the third, an estimate of the concentration may be made by observing at which step the blackening of the investigated line reaches a standard arbitrarily set value.

The spectrum may be photographed in a series of steps of graduated intensity by placing an absorption step-weakener immediately in front of the spectrograph slit. Rotating step-sectors or mesh screens cannot be used with spark sources for this purpose, because the intensity of the light radiated by the atoms of the sample decreases with time during the exposure. Each problem which one encounters may require a step-weakener of special characteristics, and it is therefore of advantage to the spectroscopic analyst to have a means of quickly preparing a step-weakener of any required design.

This paper describes a method for preparing step-weakeners of antimony. The metal is deposited on a suitable surface (*e.g.* glass or quartz) by thermal decomposition of the gaseous trihydride in a tube in which the progress of

[1] *Manuscript received July 9, 1937.*
Contribution from the Physics Department, McGill University, Montreal, Canada.
[2] *Research Associates.*

the deposition may be estimated visually or measured objectively. The apparatus required is simple and readily available in any laboratory, and a "multi-step" weakener may be made in from 15 to 20 min. The metallic films so produced are nearly neutral below λ 4000Å, and are quite uniform in density. They are strong, and no gross changes in appearance or marked changes in absorption have been observed during the three months of use which the writers have given them.

The choice of the quartz or glass plate on which any kind of film is deposited to form a weakener is important, because interference occurs between internally reflected rays in the transmitted light, except when the plate is accurately plane parallel. If the plate is badly chosen, the photographic images of the spectrograph slit exhibit intensity maxima and minima along their length, and cannot be used for intensity determinations of the highest accuracy. A consideration of the theory of such interference as worked out by Pahlen (1) suggests several ways in which this difficulty may be overcome. Perhaps the best of these is to deposit the film on a wedge-shaped plate, which is then cemented to a similar plate with Canada balsam in order to protect the film and compensate for ray deviation.

1. Deposition of the Film

The tube used for depositing the films is shown in Fig. 1. It consists of a Pyrex tube of about 3 cm. diameter drawn down to a fine jet, *J*, at one end, and closed at the other by means of a rubber cork through which runs an adjustment screw, *A*. Two side arms are blown on this tube; one is closed by the window, *W*, and the other by a rubber cork and the Pyrex tube carrying the furnace, *F*. A metal carriage, *C*, is firmly fixed in the tube so that the hole in it is directly over the furnace. The details of the water cooling for this carriage are not shown in the diagram. A flat metal slide, *E*, runs in grooves in the carriage, and may be removed from the tube by withdrawing the cork and simply pulling it out. This slide is about 2 cm. wide and 11 cm. long, and there is an opening in it which coincides with the opening in the carriage when the slide is in position. Two microscope cover slips, *M*, are fixed adjustably to the slide by spring clips so that their ends project over the opening in the slide, but leave an open strip equal to the width of the metallic film which it is desired to deposit. In addition, a metal block which carries the spring, *S*, and the adjustment

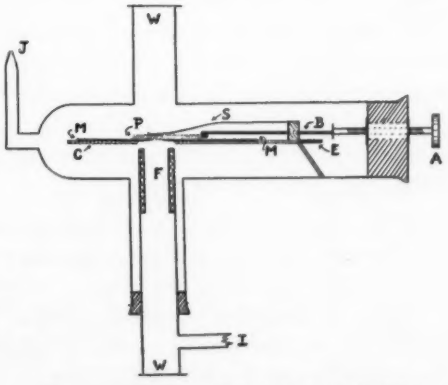


FIG. 1. *Diagram of the tube for depositing antimony films.*

rod, *B*, is permanently fixed to the slide. The quartz or glass plate, *P*, on which it is desired to deposit a film is placed on the slide as shown. It is held down on the mask, *M*, by the spring, and can be moved along the tube by adjustment of the screw, *A*.

A steady flow of a mixture of hydrogen and antimony trihydride is passed into the tube at *I*, and the escaping gas is burned at *J*. When the furnace is electrically heated to a sufficiently high temperature the antimony trihydride is decomposed and metallic antimony is deposited on the strip of the plate *P* which is left uncovered. When the density of the film is sufficiently great, the plate is moved along to the required position for the next step by adjustment of *A*, and a second film is deposited. Any number of steps of any reasonable width, and of any optical density, may be made in this way. The optical density of the film may be viewed by transmitted light at any time during the deposition by looking down through the window of the side tube. If necessary, the density may be measured objectively, but the writers have found visual estimates sufficient for their work thus far.

It should be pointed out that antimony trihydride is poisonous, and that care should be taken not to inhale appreciable quantities of it.

The furnace. The furnace is cylindrical in form with a diameter of about 1 cm. and a length of about 3 cm. The upper end of the furnace comes to within about 4 mm. of the surface of plate *P*. The heating element is wound on an aluminium cylinder, and is carefully covered with an asbestos cement. The cylinder cannot be made of a metal which forms an antimonide when heated (*e.g.*, copper), for then practically all the antimony is held by the furnace. The resistance of the furnace is about 7 ohms, and the current required is about 4 amp. The temperature has not been measured, but it must be sufficiently high to decompose antimony trihydride, which breaks down at 150° to 200° C.

The mask. The microscope cover slips which form the mask are about 0.3 mm. thick. They are ground down (from the under side) to a sharp edge with an angle of about seven degrees. This is done to get rid of projecting edges which disturb the lines of flow of the impinging gas which carries the metallic antimony. If it is not done the deposition is greater in the centre of the strip than near the edges.

The production of antimony trihydride. An ordinary Kipp generator containing dilute sulphuric acid and zinc, and a small amount of an antimony salt, is suitable for producing the mixture of hydrogen and antimony trihydride required. In practice 10 cc. of a 3 gm. per cent antimony solution was introduced into the zinc chamber of the generator, and generally no more was added during the life of the charge. The yield under these conditions was found by analysis to be from 0.006 to 0.02 volumes per cent antimony

trihydride in hydrogen. The gas was bubbled through lead nitrate to remove hydrogen sulphide, which if present resulted in the formation of yellow powdery films (sulphides of antimony). It was then passed through a calcium chloride drying tube, and into the tube proper. The rate of flow of gas generally used was about 7 cc. per sec. The gas was always allowed to flow through the tube for a few minutes before the furnace was turned on, in order to wash out the oxygen. If this was present in appreciable quantities whitish powdery films were formed (oxides of antimony).

2. Properties of the Films

Appearance, strength, and permanency. The films are metallic in appearance, and when thick enough make excellent mirrors. An enlargement of a four-step weakener is shown in Plate I, *a*. The films are strong enough for all practical purposes, and may be cleaned without damage by swabbing with cotton wool dipped in some suitable cleaning liquid. They appear to be quite stable, as might be expected from a consideration of the chemical properties of antimony. The authors have not detected any signs of cracking or other gross change, or of marked change in the absorbing power, during the three months in which the films have been in use.

Uniformity. If proper precautions are taken, as mentioned in the preceding section, the films are quite uniform in density. This point is illustrated by the transmission measurements for a four-step weakener given in Fig. 2.

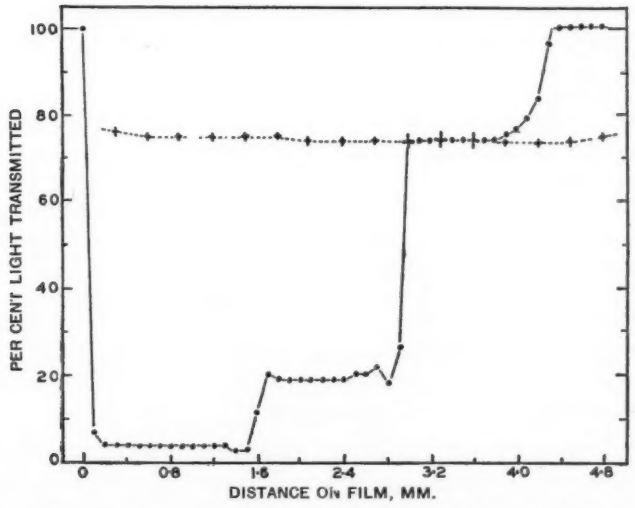


FIG. 2. *Degree of uniformity in the optical density of the steps of a four-step weakener. The points indicated by ● represent measurements taken across the steps; those indicated by + represent measurements taken along the length of a step.*

Wave-length absorption characteristics. The films are nearly neutral below λ 4000Å, but absorb less strongly for longer wave-lengths. The results of photographic transmission measurements made on two films are given in Fig. 3.

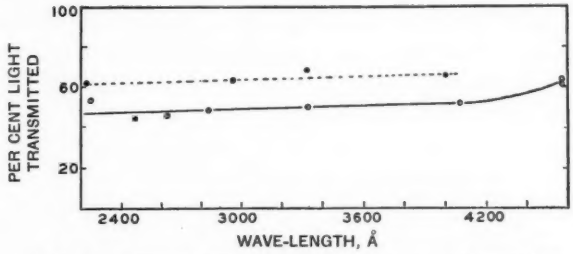


FIG. 3. *Transmission-wave-length curves for antimony films.*

3. The Construction of Absorption Weakeners

In the early stages of this work it was observed that the spectral lines almost always exhibited intensity maxima and minima along their length when thin microscope cover slips (with or without metallic films) were placed before the spectrograph slit. Subsequent investigation indicated that these effects were due to interference between internally reflected rays. Plate II, *a* and *b* illustrate the type of effect observed.

It is obviously out of the question to photometer lines consisting of distinct intensity maxima and minima with the expectation of attaining a high degree of precision in the intensity measurements. Moreover, in the use of a wedge-weakener the validity of intensity measurements depends on the validity of the assumption of a one-to-one correspondence of points on the line with points on the wedge. If interference occurs this correspondence is effectively destroyed, at least to an extent determined by the separation of the maxima. It is, therefore, important to devise a means of overcoming this difficulty. It is rather surprising that there appears to be no mention of it in the literature on absorption weakeners.

The theory of the interference phenomena which occur when light is transmitted through thin plates has been worked out by Pahlen (1). When a bundle of approximately parallel light rays is incident at an angle ϕ on a thin wedge-shaped plate of mean thickness D and angle ϵ (with the plane of incidence perpendicular to the end of the wedge), sharp interference patterns are expected at a distance E from the plate surface, such that,

$$E = \frac{D}{\epsilon} \frac{\sin \phi \cos^2 \phi}{\eta^2 - \sin^2 \phi} \tag{1}$$

where η is the refractive index of the plate material. This interference plane passes through the apex of the wedge at an angle α with the wedge surface, where,

$$\tan \alpha = \frac{\sin \phi \cos^3 \phi}{\eta^2 - 1 + \cos^4 \phi} . \tag{2}$$

Sharp interference will also be found in planes parallel to this one and at distances e_ρ from it, where,

$$e_\rho = \frac{\lambda}{2\epsilon^2} \cdot \frac{\sin \alpha}{\sin \phi \cdot \cos (\phi - \alpha)} \cdot \rho \qquad \rho = \pm\tfrac{1}{2}, \pm 1, \pm\tfrac{3}{2}, \ldots \qquad (3)$$

The interference is virtual when ρ is negative. When $\phi = 0$,

$$e_\rho = \frac{\lambda}{2\epsilon^2\eta^2} \rho \ .$$

In all these planes the interference maxima will be separated by a distance h, whose projection, s, on a plane normal to the direction of the rays will be,

$$s = \frac{\lambda}{2\epsilon} \frac{\cos \phi}{\sqrt{\eta^2 - \sin^2 \phi}} \ . \qquad (4)$$

These equations describe qualitatively the effects that have been observed, but the authors have made no attempt to test them in an absolute quantitative sense. The following table, calculated by means of the above equations, shows the expected magnitude of the various variables for interference in a quartz plate.

TABLE I

ϵ, sec.	ϕ, min.	D, cm.	E, cm.		$e_{\frac{1}{2}}$, cm.		s, mm.	
			λ1980	λ5890	λ1980	λ5890	λ1980	λ5890
10	10	.03	.64	.75	740.	2250.	1.2	3.8
		.3	6.4	7.5	740.	2250.	1.2	3.8
	180	.03	11.3	13.4	740.	2250.	1.2	3.8
		.3	113.	134.	740.	2250.	1.2	3.8
3600	10	.03	.0018	.0021	.0059	.020	.0034	.011
		.3	.018	.021	.0059	.020	.0034	.011
	180	.03	.033	.038	.0059	.020	.0034	.011
		.3	.33	.38	.0059	.020	.0034	.011

The theoretical considerations suggest that there are three ways in which the undesired effects may be eliminated; (1) by using an accurately plane parallel plate on which to deposit the film, (2) by using a "thick" plate at an appreciable angle of incidence so that the first interference plane falls some distance behind the spectrograph slit, and (3) by using a wedge-shaped plate of sufficiently large angle to bring the interference maxima so close together that they are not resolved by the grain of the photographic plate.

The first of these alternatives is apt to prove expensive. In accordance with the second, the authors have successfully made weakeners which are useful down to λ 3000Å. The required film is deposited on a microscope cover slip, which is then cemented to a metal ring to form one side of a water cell. A second cover slip without a film is cemented to the other side of the

ring to form the complete cell. This is filled with water and sealed off. Its disadvantage is that the film is unprotected. When the film was coated with a pyroxalin solution such as is used for rock salt prisms serious interference effects occurred owing to internal reflections from the pyroxalin-air and pyroxalin-metal surfaces. It is questionable whether the success of these weakeners is due to their thickness or to the fact that the angle between the two external surfaces is appreciable. Some pieces of quartz 3 mm. thick caused striking interference patterns; this rather inclines one to the latter view. Moreover, if by chance such a weakener is set up at exactly normal incidence, the first interference plane will lie directly on the surface, and if this is against the slit, interference phenomena should be observed in the photograph.

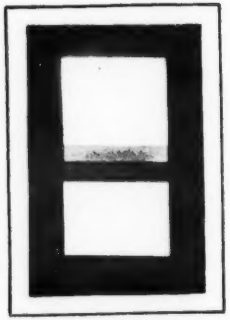
Probably the best method of construction is that of the third alternative. The film is deposited on a wedge-shaped plate of angle, say, 3°. The separation of the interference maxima will be 0.0022 mm. for λ 5890Å, and this distance will not be resolved on the photographic plate with a spectrograph of ordinary magnification. In order to protect the film and to compensate for ray deviation, a second similar plate without a film is cemented to the first. This construction was found to be entirely satisfactory.

Acknowledgment

The authors are indebted to the Rockefeller Foundation for financial assistance.

Reference

1. PHALEN, E. V. D. Ann. Physik, 39 : 1567-1589. 1912.



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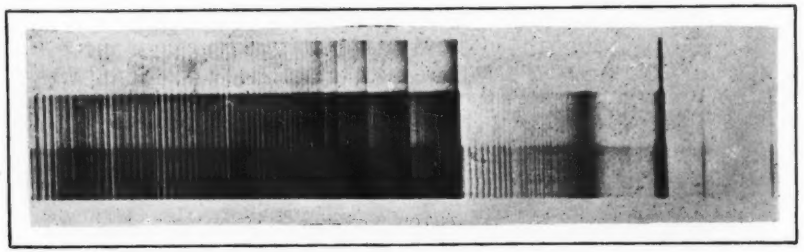

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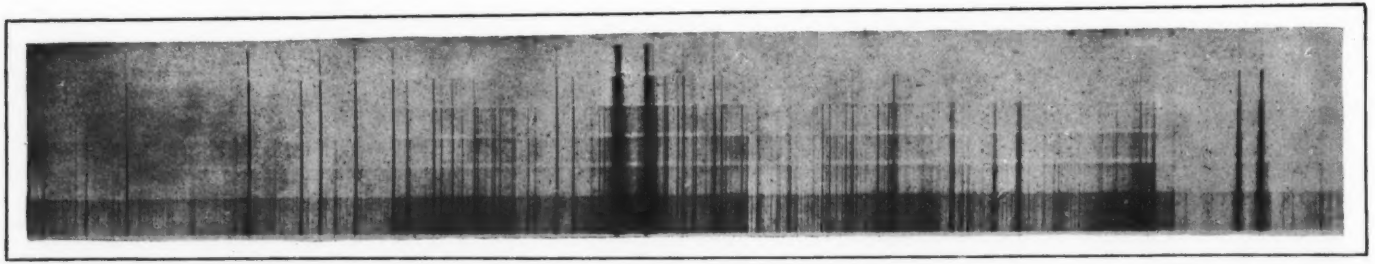
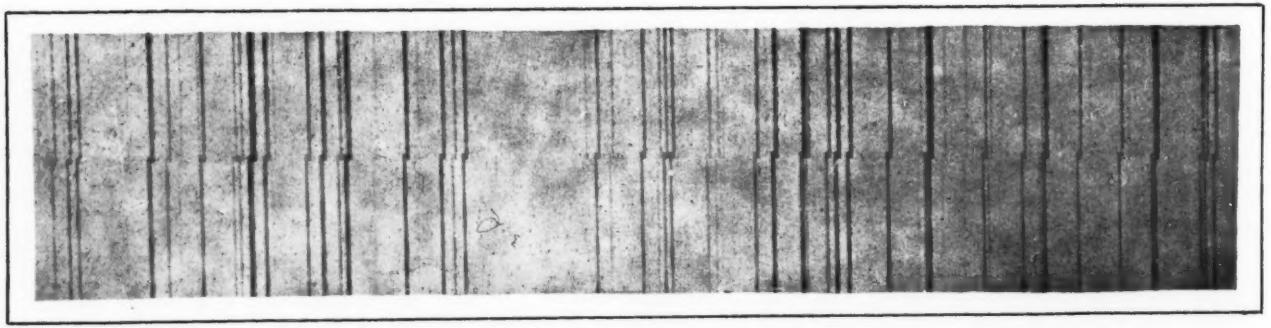


c

a. A photograph of a four-step weakener. The actual width of each of the steps is about 1.2 mm. b. The spectrum of the cyanogen bands at λ 3883Å taken with a three-step weakener. c. The spectrum of the copper arc from λ 2860 to 4100Å taken with a six-step weakener. The strong lines in the centre are, 3247.6 and 3247.0 Å.

PLATE I



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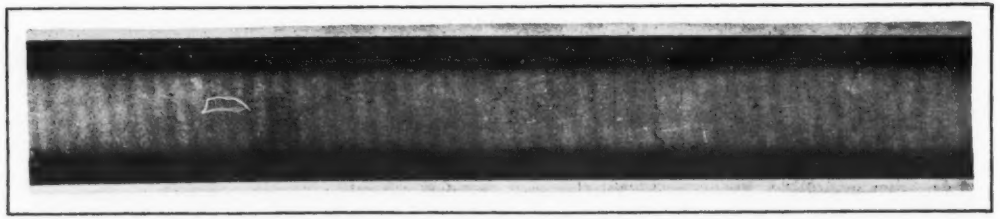

b

a. Two exposures showing interference effects in line spectra. These effects are of the type discussed in Section 3. They were obtained by placing an ordinary microscope cover slip (without a film) before the slit of the spectrograph. The direction in which the cover slip showed a deviation from plane parallelism was determined, and for the first exposure this direction was set parallel to the length of the spectrograph slit. For the second exposure the cover slip was rotated through a fairly large angle from the first position. In both exposures the surface of the cover slip was kept perpendicular to the collimator axis. The interference maxima in the first exposure are much closer together than in the second exposure, which is in accord with theoretical expectations. The region of the spectrum shown in the photograph is near λ 3700Å. The magnification of the enlargement is about 5×. An interesting feature shown in this plate is the rather rapid change in the spatial position of a maximum when the wave-length is changed. (See Pahlen's article.)

b. Interference effects in the continuous spectrum emitted by a band lamp. These effects were obtained when a cover slip was placed before the spectrograph slit. They undoubtedly have an explanation based on the considerations of Section 3. The less exposed strip in the centre of this photograph is due to the absorption of the antimony film which was deposited on the cover slip. The spectral region shown is near λ 3600Å. The magnification of the enlargement is about 5×.

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THE EFFECT OF ALCOHOLS ON THE TIME OF SET OF ALKALINE SILICA GELS[1]

BY L. A. MUNRO[2] AND C. A. ALVES[3]

Abstract

Measurements have been made of the decrease in time of set of alkaline silica gels induced by a series of alcohols and acetone. Acetone, propyl, and butyl alcohols caused a marked increase in pH of the gel during setting. Glycol has a much smaller effect on setting time than the monohydric alcohols, while with glycerol the time of set of the alkaline gels was actually increased. Time of set is not strictly paralleled by the dielectric constant.

It has been shown by Hurd and Carver (2) that ethyl alcohol, acetaldehyde, and acetone increased the time of set of silica gels. Glycerol had only a negligible effect. This delayed setting was observed for gels having a pH range of from 5.2 to 6.0. Prasad and Hattiangadi (7) have also determined the effect of methyl, ethyl, and propyl alcohols, and acetone on the time of set of acid and alkaline gels. With alkaline gels these investigators observed an effect opposite to that obtained with acid gels *viz.*, a decrease in the time of set. It is true that certain substances, the alkyl-amines, pyridine, and ammonia did decrease the time of set of acid gels, but it was noted that these increased the pH of the gel (2). Prasad (6) has shown that silica gels have a minimum time of set at about pH 7.6, the setting time increasing rapidly on each side of this optimum pH. Accordingly, any reagent that brings the pH of the acid gels nearer the isoelectric point would decrease the time of set. The alcohols, acetaldehyde, and acetone did not change the pH of Hurd and Carver's acid gels, so the alteration of the time of set was attributed to an effect of the addition agent alone.

During class experiments in the colloid laboratory it was noted, however, that the pH of alkaline gels was increased by the above substances. With these pure addition agents which had no effect on the pH of acid gels, an initial increase in pH was observed, and the final value on setting was appreciably different from that of the water gel. An increase in pH of an alkaline gel would be expected to increase the time of set (6). Prasad did not note any change in pH on addition of non-electrolytes to alkaline gels, but he did observe an induced decrease in the time of set. It was accordingly determined to study the effect of a longer homologous series of alcohols on the time of set of alkaline gels of known pH.

[1] *Manuscript received June 21, 1937.*
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The time of set was determined by the tilted rod method described by Hurd and Letteron (3). Such a method measures merely the time required for gels to reach a certain degree of rigidity. Prasad and Parmar (8) have pointed out that gelation probably consists of three distinct processes: (1) formation of a sol; (2) coagulation, hydration, and agglomeration; (3) structural changes in rearrangements. Since acid and alkaline silica gels are very different in their optical properties during gelation, the method of Hurd would seem to be more suitable than the optical methods recommended by Prasad.

The time of set is quite sensitive to temperature changes (1, 4). The temperature of the laboratory was accordingly regulated to within one degree of the temperature of the thermostat (20° C.). A well stirred thermostat is necessary to dissipate the heat produced in mixing the acid and silicate. The required amounts of acid, water, and addition agent were placed in 50 cc. Pyrex beakers in the thermostat. A 25 cc. portion of the standard silicate solution was pipetted into beakers that had previously held 25 cc. of silicate and had drained for six seconds. This assured delivery of a constant volume of silicate. The silicate was added to the acid solution with rapid stirring, care being taken that the whole operation involved the same length of time (10 sec.). The stop watch was started as soon as all the silicate was added. In all experiments on the alkaline gels the acetic acid used was prepared by diluting 100 cc. of glacial acetic with 500 cc. of water. Standard sodium silicate solution of sp. gr. 1.1563 was obtained by dissolving Baker's c.p. "crystalline" sodium silicate. This solution contained 6.6% of silicon dioxide. It was diluted with distilled water to give a solution containing 3.3% of silica. Addition agents were of Eastman's best grade.

The attempted use of the antimony electrode for the pH determinations was abandoned, as it has been shown by Kolthoff and Hartong (5) that this gives incorrect readings unless the medium is stirred continuously. As all the writers' experiments were carried out in alkaline solution, the quinhydrone method used by Hurd and Carver (2) for acid gels could not be employed either. The pH of the writers' gels was estimated by means of indicators. The time of set and pH were determined in portions of the same mixture. No indicator was added to the portion upon which determination of the time of set was carried out; this avoided any influence of the indicator itself on the time of set.

The initial pH was 10.4 in all cases in which the amount of added substance was 0.5 cc. This increased to 10.5 with higher concentrations. The pH was found to change on setting—the pH of the water-acetic acid gel increasing to 10.6, while with acetone and *n*-propyl alcohol the final pH changed from 10.6 to 11.2 as the amount of added substance was increased to 2.0 cc. The effect of addition agents on the pH of the gel as determined colorimetrically is illustrated by Table I and the results for the alcohols studied are given in Table II.

ERRATUM

Page 354, second paragraph, line 13, for "100 cc." read "50 cc."

TABLE I

CHANGE IN FINAL pH WITH BUTYL ALCOHOL AND ACETONE AS ADDITION AGENTS

Cc. added	Tert. BuOH (22° C.)			Acetone (Table III)	
	Time of set, sec.	Initial pH	Final pH	Initial pH	Final pH
0.0	240	10.0	10.5	10.4	10.6
0.5	120	10.4	10.6	10.4	10.7
1.0	80	10.4	10.6	10.5	10.8
1.5	55	10.4	10.6	10.5	11.0
2.0	40	10.4	10.6	10.5	11.2

TABLE II

Concentration of added substance		Time of set, sec.	Concentration of added substance		Time of set, sec.
Cc. in 50 cc. gel	Moles per l.		Cc. in 50 cc. gel	Moles per l.	
Methyl alcohol			*n-Propyl alcohol*		
0.0	0.0	210	0.0	0.0	210
0.5	.248	134	0.5	.134	116
1.0	.50	103	1.0	.27	69
1.5	.74	86	1.5	.40	43
2.0	.99	64	2.0	.54	32
2.5	1.24	50	2.5	.67	21
3.0	1.49	44	3.0	.80	9
Ethyl alcohol			*Iso-propyl alcohol*		
0.0	0.0	210	0.0	0.0	214
0.5	.172	115	0.5	0.131	108
1.0	.34	74	1.0	.26	68
1.5	.52	49	1.5	.39	42
2.0	.69	31	2.0	.52	30
2.5	.86	22	2.5	.66	18
3.0	1.03	15	3.0	.79	10
n-Butyl			*Sec-butyl*		
0.0	0.0	210		0.0	214
0.5	.109	120		.109	123
1.0	.22	67		.22	65
1.5	.33	42		.33	39
2.0	.44	30		.44	21
2.5	.55	19		.55	14
3.0	.65	14		.65	ppt.
Iso-butyl			*Tert-butyl*		
0.0	0.0	212		0.0	215
0.5	.11	114		.106	110
1.0	.22	67		.21	64
1.5	.33	42		.32	39
2.0	.44	28		.42	21
2.5	.55	ppt.		.53	ppt.

Fig. 1 shows the data for Table II; the time of set for similar volumes of added substance is plotted for individual members. The curve obtained for 0.5 cc. of added substance is quite irregular. However, the curves for higher

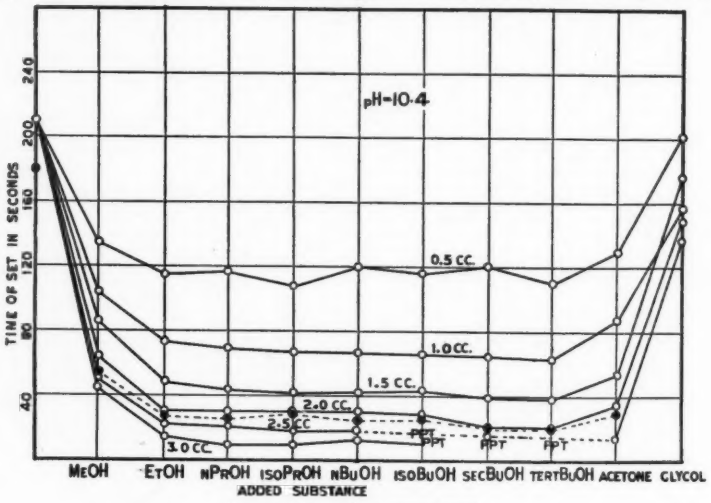

FIG. 1; ●, earlier experiment.

concentrations show regular gradation in effects; this indicates that the effect of changes in pH is less than the specific effect of the addition agent. The order of effects for similar volumes seems to be:— tert. BuOH = sec. BuOH > iso-, *n*-, BuOH, *n*- and iso-PrOH > EtOH > acetone > MeOH. The same order is shown within experimental error in a previous experiment on the addition of 2 cc. of addition agents to a gel having a setting time of 180 sec. at 18° C. This is shown graphically by solid points and broken line, Fig. 1.

For the higher concentrations of the butyl alcohols, an amorphous precipitate was formed instantaneously with sometimes subsequent coagulation of the supernatant sol. In Figs. 2 and 3 the times of set are plotted against molar concentrations, calculated from the specific gravity and molecular weight.

TABLE III

Added substance, cc.	Acetone		Glycol		Glycerol	
	Moles per litre	Time of set, sec.	Moles per litre	Time of set, sec.	Moles per litre	Time of set, sec.
0.0	—	210	—	215	—	216
0.5	0.137	129	0.179	202	0.137	244
1.0	.274	87	.358	166	.274	250
1.5	.411	54	.537	156	.411	253
2.0	.548	34	.716	149	.548	255
2.5	.685	14	.895	137	.685	260
3.0	.822	ppt.	1.074	136	.822	265

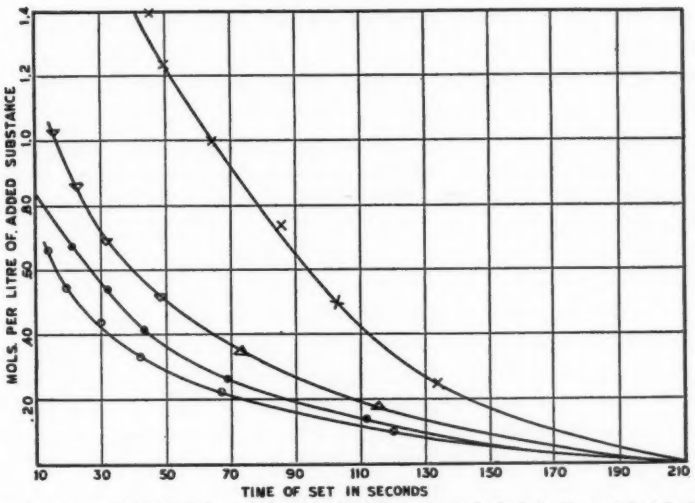

FIG. 2. ×, *methyl alcohol;* △, *ethyl alcohol;* ●, *n-propyl alcohol;* ○, *tert. butyl alcohol; pH, 10.4.*

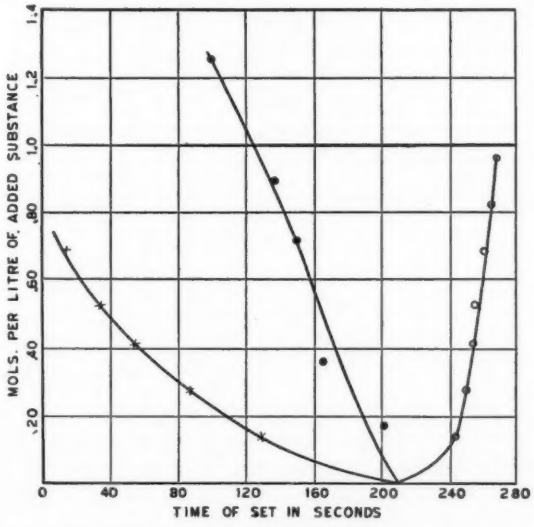

FIG. 3. *pH, 10.4;* ×, *acetone;* ●, *ethylene glycol;* ○, *glycerol.*

The most striking results of this investigation are: (1) the small effect of glycol as compared with that of acetone and propyl alcohol, compounds of similar molecular weight; and (2) the actual reversal of the effect as shown by glycerol (Table III).

It has been noted by Hurd and Carver (2) that glycerol has a very slight effect on the time of set of acid gels. Their observation has been checked in

the case of a very slow setting gel of pH 5.1 from silicate containing 3.3% silicon dioxide (Table IV).

There is, therefore, a slight increase in the time of set in acid gels which is apparently not proportional to the concentration.

The change in time of set induced by the addition agents is approximately parralleled by the gradation of the dielectric constants in this series. A change in the dielectric constant of the dispersion medium would influence the electrical layer and hence the stability of the sol. It is known that a negative sol can be changed to a positive one by the addition of alcohol (7). The observed change in pH of the writers' alkaline gels with the addition of non-electrolytes may be due in part to the changed dielectric properties.

There are, however, several anomalies which, as Prasad points out (7), "cannot be explained by the diminution of the dielectric constant and hence change in density of the charge on the particle." The discrepancies quoted by him may be supplemented from the present investigation. Acetone and *n*-propyl alcohol have almost identical dielectric constants at 20° C., but have dissimilar effects on the time of set. Isobutyl and tertiary butyl alcohols should show a greater divergence in the time of set.

The behavior of glycerol cannot be accounted for by the retarding effect of greater molecular size. If such were true a similar increase in time of set would be observed with acid gels. Table IV shows that this is not the case.

TABLE IV

Expt.	Added substance, cc.	Time of set, hr.	sec.	Expt.	Time of set, hr.	sec.
1	0.0	13	30	7	13	35
2	1.0	13	53	8	13	50
3	2.0	13	55	9	13	50
4	3.0	14	0	10	14	03
5	4.0	14	0	11	14	0
6	5.0	13	55	12	13	58

Weber and Lederer (9) have recently determined the dehydrating power of addition agents. Gelatin gels were treated with a series of alcohols and the amount of dehydration was measured. Monohydric alcohols were found to withdraw water in the order, PrOH, EtOH, MeOH. This is the same order as their effect on the time of set. Glycols were observed to have a stronger dehydrating action than the monohydric alcohols, and the effect became greater with increase in molecular weight and number of hydroxyl groups in the higher alcohols. If the effect of addition agent on the time of set is due to dehydration of the micelles, one might expect on the basis of their experiments a very short setting time with glycol and glycerol.

It would seem that the anomalous behavior of glycerol would justify further study.

References

1. HURD, C. B. J. Phys. Chem. 40 : 21-26. 1936.
2. HURD, C. B. and CARVER, D. H. J. Phys. Chem. 37 : 321-329. 1933.
3. HURD, C. B. and LETTERON, H. A. J. Phys. Chem. 36 : 604-615. 1932.
4. HURD, C. B. and MILLER, P. S. J. Phys. Chem. 36 : 2194-2204. 1932.
5. KOLTHOFF, I. M. and HARTONG, B. D. Rec. trav. chim. 44 : 113-120. 1925.
6. PRASAD, M. and HATTIANGADI, R. R. J. Indian Chem. Soc. 6 : 893-902. 1929.
7. PRASAD, M. and HATTIANGADI, R. R. J. Indian Chem. Soc. 6 : 991-1000. 1929.
8. PRASAD, M. and PARMAR, M. U. Current Sci. 4 : 310-311. 1935.
9. WEBER, L. I. and LEDERER, F. Biochem. Z. 285 : 115-122. 1936.

THE PREPARATION OF PURE METHANE FROM NATURAL GAS[1]

By E. H. Boomer[2], C. A. Johnson[3], and V. Thomas[4]

Abstract

A method of removal of all hydrocarbons in natural gas other than methane is described. Pyrolysis of the higher hydrocarbons under such conditions of temperature and rate of flow that methane is not affected is used. The products of pyrolysis are easily removed by common chemical methods.

Introduction

It was necessary for the work proceeding in these laboratories, that a fairly large supply of gas be available consisting only of methane with a small proportion of nitrogen. Natural gas that is high in methane, containing about 3.5% higher hydrocarbons and 5.7% nitrogen was available from the Viking field. The usual method of separating the methane by liquefaction and distillation was not practicable under the circumstances, and another method, based on experience obtained in experiments on pyrolysis, was devised. Briefly, the method consisted of controlled pyrolysis of the natural gas, resulting in the decomposition of all hydrocarbons but methane, followed by removal of the decomposition products. The method has been applied to Viking natural gas only, but is applicable to any natural gas. The presence of sulphur compounds in the gas is not detrimental, and the sulphur is removed completely in the process. It is necessary only to determine, by means of a few experiments, the temperature and rate of flow that produces decomposition of all hydrocarbons other than methane. The method is presented as an alternative to the use of low temperature distillation in the separation of methane from natural gas. In the event that nitrogen is undesirable, separation by liquefaction must be employed.

Apparatus and Operation

The supply of natural gas was connected to the apparatus shown in Fig. 1 through the flowmeter *A*. The rate of flow of gas was regulated by the stopcock shown. The drying tower, *B*, contained calcium chloride and served to remove water vapor from the gas. The gas then entered a quartz pyrolysis tube, $\frac{3}{4}$ in. in diameter, heated over a 12 in. length by means of an electric furnace. The tower, *D*, contained glass wool which acted as a filter and removed most of the suspended carbon and oily matter formed in the gas during pyrolysis. The next tower, *E*, contained soda-lime, and it removed hydrogen sulphide formed in the pyrolysis of organic sulphur compounds

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in the natural gas. Activated coconut charcoal, placed in the large bottle, *F*, removed the vapors of liquid hydrocarbons such as benzene and considerable quantities of the heavier, unsaturated gaseous hydrocarbons produced on pyrolysis. From *F* the gas entered the bottom of the sulphuric acid scrubber,

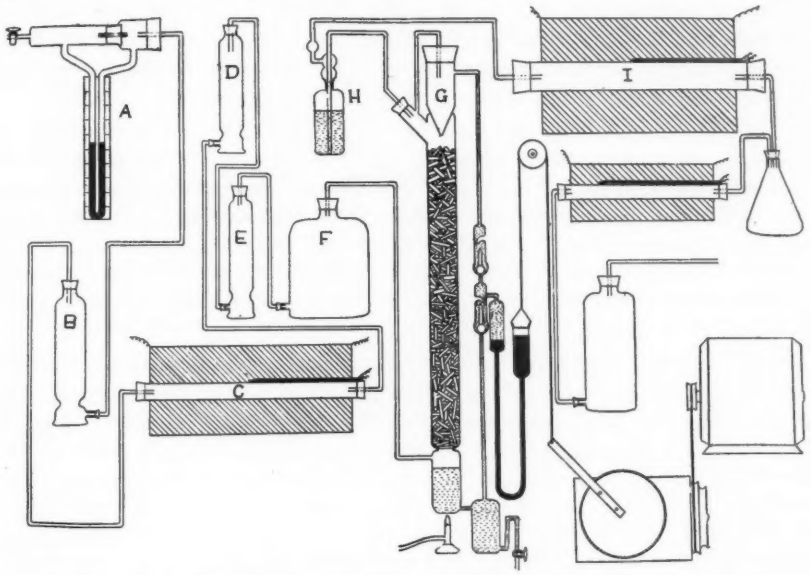

FIG. 1. *Apparatus for pyrolysis and removal of higher hydrocarbons in natural gas.*

G. The tower was packed with short pieces of glass tubing and was charged with 400 cc. of 95% sulphuric acid containing 1% of silver sulphate. The acid was heated to about 70° C. by means of a gas burner and was circulated continuously through the scrubber by means of the glass and mercury pump shown. Olefines and other unsaturated compounds in the gas, as well as sulphur compounds, were removed completely by the sulphuric acid and some sulphur dioxide was produced. The scrubber, *H*, containing sodium hydroxide solution, removed any sulphur dioxide in the gas. The gas passed next through two copper oxide tubes, *I*, heated electrically to 320° C. Here, hydrogen and carbon monoxide were oxidized to water and carbon dioxide respectively. Two copper oxide tubes were necessary with a water trap between them to ensure complete removal of hydrogen and carbon monoxide. The first tube contained about five pounds and the second tube about one pound of copper oxide. The carbon dioxide was removed by soda-lime in the bottle shown. The gas, now methane, was stored in water-sealed gas holders.

A series of experiments showed that at 780° C., all the ethane and heavier hydrocarbons were decomposed in the pyrolysis tube; this process yielded olefines, aromatics, carbon, carbon monoxide, and hydrogen. In addition, the sulphur compounds in the gas were converted largely to hydrogen sulphide.

The rate of flow as measured on the flowmeter, *A*, could be as much as 1000 cc. per min. but could not be less than 800 cc. per min. without some decomposition of methane taking place. The Viking gas used here was of the same composition as that described above and contained some ten grains of sulphur per 100 cu. ft. This yielded a gas free from sulphur; its composition was: methane, 94.5; nitrogen, 5.5%. There were only slight variations from this composition corresponding to variations in the temperature of the pyrolysis tube.

The apparatus, while of many parts, was quite simple to operate. It required no attention other than that required for replacement of chemicals, and was operated 24 hr. per day. The average production of gas per day was 40 cu. ft. Once a day the sulphuric acid was replaced, and once every ten days the calcium chloride, soda-lime, and sodium hydroxide scrubbers were refilled. About once a month the copper oxide was re-oxidized by passing air through the tubes, and the coconut charcoal was activated by steam treatment.

The consumption of materials per 100 cu. ft. of gas prepared was as follows: 1000 cc. technical, 95%, sulphuric acid, 50 gm. calcium chloride, 80 gm. soda-lime, and 20 gm. sodium hydroxide. Approximately 1500 watts of electric power were required to heat the furnaces.

THE PRECISION COMBUSTION ANALYSIS OF GASES[1]

By E. H. Boomer[2] and C. A. Johnson[3]

Abstract

A precise method of determining the hydrogen and carbon content of gases is described. The method employs, in part, the methods of ultimate organic analysis by combustion over copper oxide and collection of the carbon dioxide and water formed. It is particularly suited to the analysis of combustible gases containing vapors of volatile liquids.

Introduction

In connection with other work proceeding in these laboratories it was necessary to analyze quantitatively gas mixtures, substantially methane, containing small amounts of hydrocarbon vapors. A procedure involving distillation or freezing out of the vapors was not practicable, and owing to the small amounts of vapors present the usual combustion analysis on the Orsat type of apparatus was quite inadequate.

A method of analyzing such mixtures to give precisely the carbon and hydrogen content was devised. This method is applicable to any gas for which such information is sought. The principles employed are those used in ultimate analysis by combustion for carbon and hydrogen as commonly practised with liquids and solids. Briefly, the method consists in oxidizing a measured sample of gas in a closed system to carbon dioxide and water, which are collected and weighed in the usual absorption vessels. Hot copper oxide, plus 1% of cerium oxide as promotor, served as the oxidizing agent. As is well known (1, Chap. 13) the rate of oxidation of methane by copper oxide is slow, and, while cerium oxide speeds up the reaction appreciably, provision has to be made for recirculation of the gases. Experiments showed that several minutes contact was necessary when the copper oxide was at 800° C. Finally, to ensure complete oxidation to carbon dioxide and water, oxygen was admitted to the circulating system. In order to handle gases containing sulphur or nitrogen compounds, the usual additions of a reduced copper spiral and granulated lead chromate to the combustion tube may be made. This report covers the procedure necessary in the absence of sulphur or nitrogen compounds.

The method was given a rigorous test by analyzing known mixtures of methane, nitrogen, and benzene vapors. The deviations between the calculated and observed weight percentage of benzene and methane was less than 0.5%, and on unknown gas mixtures duplicates were obtained showing similar agreement.

[1] *Manuscript received May 31, 1937.*
Contribution from the Chemical Laboratories of the University of Alberta, Edmonton, Canada, with financial assistance from the National Research Council of Canada.
[2] *Associate Professor of Chemistry, University of Alberta.*
[3] *Research Assistant, Associate Committee on Gas Research, National Research Council, 1934-1936. Present address: 513 Beacon Street, Boston, Mass.*

The errors were controlled principally by the weight of carbon dioxide and water; any errors in these data, which are correct to within 0.1 mg., being magnified in the process of calculation. While a high degree of precision is unnecessary in the application for which the method was devised, the precision of the analysis can be improved simply by using larger gas samples.

Apparatus

The apparatus is shown in diagramatic form in Fig. 1. The gas sample was measured in the calibrated pipette *C*. The pipette volume, at 25° C., was 183.93 cc. The temperature was determined by means of a calibrated

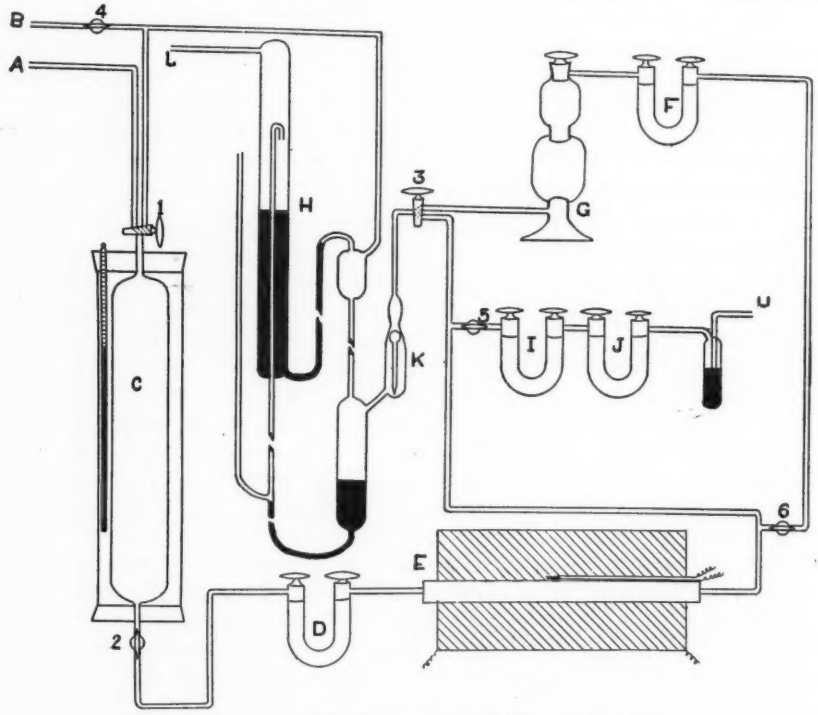

FIG. 1. *Apparatus for precision combustion analysis of gases.*

thermometer immersed in a water jacket surrounding the pipette. The pressure was measured by means of a mercury manometer connected to a gas storage system (not shown), which was connected at *A*. The whole apparatus could be evacuated by mercury diffusion pumps connected at *B* through stopcock 4. A modified Sprengel pump, *H*, was employed to circulate the gas in the apparatus. This pump was operated automatically from a water jet pump attached to *L*. A check valve, *K*, acted as a trap against mercury spray and prevented entrance of mercury to the rest of the apparatus

in the event of failure of the evacuating system. The copper oxide tube, *E*, 15 in. long and $\frac{3}{4}$ in. in diameter held about 200 gm. of copper oxide-cerium oxide mixture. The quartz tube was protected from the action of hot copper oxide by a lining of thin asbestos paper. The temperature of the copper oxide was maintained at $800° \pm 10°$ C. by means of an electric furnace as shown, the temperature being indicated by means of a milli-voltmeter and thermocouple. This temperature was sufficiently high to oxidize rapidly and completely the hydrocarbons in the gas.

A magnesium perchlorate drying tube, *D*, which absorbed the water produced on combustion, was placed immediately after the combustion tube. Provision was made for warming the connection between the combustion tube and the absorption tube. A soda-lime absorption bulb, *G*, and the guard tube, *F*, containing magnesium perchlorate, were connected on a by-pass line through stopcocks 3 and 6. An oxygen supply was connected at *U*, carbon dioxide and water being removed by soda-lime in tube *J* and by magnesium perchlorate in tube *I*.

Operation

The drying tube, *D*, and carbon dioxide absorption assembly, *G* and *F*, were weighed, filled with oxygen at atmospheric pressure, and connected to the apparatus with clean, sulphur free, pressure tubing, the joints being wired. The temperature of the combustion furnace was raised to 800° C. and the whole apparatus, except the absorption tubes, was evacuated through stopcock 4. The absorption tubes were of the type having built-in stopcocks. The mercury supply and discharge tubes connected to the Sprengel pump were shut off by screw clamps. With stopcock 2 closed and stopcock 1 opened to the gas storage system through *A*, a sample of gas was passed into the pipette, *C*, the pressure and temperature being recorded. With stopcocks, 3, 4, 5, and 6 closed, stopcock 1 reversed and stopcock 2 open, the gas sample was allowed to expand into the apparatus. The level of the mercury reservoir of the Sprengel pump was adjusted to match the gas pressure in the apparatus and circulation was then started. The rate of circulation was about 100 cc. per min., and in 15 min. oxidation of the gas was nearly complete. Circulation was stopped momentarily, stopcock 3 reversed, and 6 opened to put the carbon dioxide absorber in the circulating system. Stopcock 5 was opened and oxygen allowed to flow into the system. After adjusting the level of the mercury reservoir of the Sprengel pump to match atmospheric pressure, circulation was started again. Oxygen entered the system automatically as the remaining traces of combustible gases were oxidized and the copper was reoxidized. After 45 to 60 min., the absorption systems were removed and weighed.

For gases containing only three components, the carbon-hydrogen analysis obtained above in conjunction with a density determination permitted the calculation of the composition. An analysis took from 1.5 to 2.0 hr. but of this time less than half an hour was actually consumed in making adjust-

ments and weighings. Little experience is required to obtain excellent results. It is essential, of course, to have no leaks in the system and to take the usual precautions in determining the weight increases of the absorption tubes. The chief precaution necessary occurs when a combustion tube is newly installed. The tube and its contents must be heated to 800° C., or somewhat higher, while being evacuated until gas ceases to be evolved.

TABLE I

ANALYSIS BY COMBUSTION AND DENSITY MEASUREMENTS OF SYNTHETIC AND UNKNOWN MIXTURES OF METHANE, NITROGEN, AND BENZENE VAPOR

Weight per cent from make-up:								
Benzene	15.31		8.88		—		—	
Methane	74.55		79.83		—		—	
Density, gm. per litre	0.8730		0.8152		0.8551		0.8384	
Sample volume, cc. at N.T.P.	158.3	158.9	95.35	95.06	95.33	95.03	95.43	95.50
Combustion data:								
Carbon dioxide, gm.	0.3546	0.3542	0.1937	0.1931	0.2190	0.2195	0.2119	0.2115
Water, gm.	0.2479	0.2477	0.1454	0.1449	0.1551	0.1555	0.1530	0.1519
Weight per cent from analytical data:								
Benzene	15.32	15.25	8.92	8.90	15.04	15.10	13.04	13.09
Methane	74.60	74.22	79.80	79.80	79.29	79.75	80.40	80.12

Reference

1. DENNIS, L. M. Gas analysis. Macmillan Co., N.Y. 1919.

EQUILIBRIA IN TWO-PHASE, GAS-LIQUID HYDROCARBON SYSTEMS

I. METHODS AND APPARATUS[1]

By E. H. Boomer[2], C. A. Johnson,[3] and G. H. Argue[4]

Abstract

An apparatus was devised by means of which a gas and a liquid could be brought into equilibrium at any desired pressure up to 370 atm. and temperatures from 25° C. to above 100° C. Provision was made for the taking of samples of known volume from the liquid and gas phases in equilibrium. Analytical methods were developed to yield phase densities and compositions.

Introduction

A knowledge of the behavior of two-phase, liquid-gas systems in equilibrium is of interest from many points of view. Particularly is this true when the behavior of such systems is determined over a wide range of pressures and temperatures. The limitations of such expressions as Henry's law and Poynting's rule are well known, and more general expressions are desirable. Simple two-component systems can be used and are of much scientific interest. Further, a study of two-component systems may form a basis for the consideration of more complex systems of equal scientific interest and greater practical interest.

The present work is concerned solely with systems formed of the simpler hydrocarbon gases and liquids. Such systems are useful in a scientific way in that the deviations from the simple ideal laws of solution become very great, and so are easily determined at relatively moderate pressures. On the practical side, investigations of such systems are useful in giving information as to conditions existing in the producing horizons of oil and gas fields. The primary reason for this work is, in fact, the study of conditions in the producing horizons of the Turner Valley oil and gas field of Southern Alberta. Because of this the systems studied were the first members of each hydrocarbon series and the actual products of the Turner Valley field. Further, such investigations as these have value in view of the trend to higher pressures in industrial practice during recent years. The information obtained may be of service in the design of processes and equipment.

Previous to the inception of this work, the literature covering the subject was relatively scanty. Most of the work dealt with only one of two phases in equilibrium, and further, the components were, in the chemical sense, quite unrelated. Some work on systems of natural gas and associated oils had

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Contribution from the Chemical Laboratories of the University of Alberta, Edmonton, Canada, with financial assistance from the National Research Council of Canada.
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appeared (1, 4, 6, 8), and Frolich had determined the solubility of methane in various organic solvents (5) at pressures as high as 200 atm. The most comprehensive work on the subject appeared in recent years as a succession of papers by Sage, Lacey, and collaborators. The first of these papers (9) described apparatus and methods. Their methods differ greatly, in general, from those developed here, and, while their field of investigation is wider, little overlapping of results occurs.

The aim of the present investigations was to devise suitable apparatus and methods, and to determine the composition and density of both phases existing in equilibrium. Single phase systems were not considered; this limits the investigation to univariant equilibria shown as lines on two-dimensional phase diagrams. The pressure was varied from atmospheric to the critical value of complete miscibility or to a maximum of 370 atm. A temperature range of 25° to 125° C. was employed, and higher temperatures may be used when desirable. The gas used was substantially methane, and the liquids comprised a number of lower hydrocarbons of each series. Present work is concerned with a complex mixture such as occurs naturally in the Turner Valley oil and gas field of Southern Alberta. This report deals solely with methods and apparatus used in examining the simple systems.

Apparatus

The apparatus comprised in its essentials, means of compressing and storing gases, the equilibrium pipettes, and analytical apparatus. The information desired for simple systems was merely the composition and density of the gas and liquid phases in equilibrium. Consequently, it was not necessary to know precisely the amounts of liquid and gas added to the equilibrium pipettes. It was necessary only to be certain that two phases existed, and that the samples of liquid and gas withdrawn for analysis were homogeneous. These conditions were fulfilled easily at the lower pressures, where the amount of liquid added could be varied relatively widely without the disappearance of a phase. At high pressures, particularly near the critical value, the allowable variation in the amount of liquid added was very much less but still appreciable. None of this is true for complex systems. In such cases, both the amount of liquid and gas added must be known.

Compression and Storage of Gases

The gases used were prepared and purified at atmospheric pressure (3) and compressed into a 15 litre storage vessel. Two gases were used, both derived from Viking natural gas; one contained some ethane and nitrogen besides methane, and the other contained only nitrogen besides methane. From the 15 litre storage vessel, *A*, Fig. 1, the gas could be taken directly to the equilibrium pipette, or compressed further by hydraulic means, depending on the pressure desired. With valves 1 and 2 open, and valve 3 closed, the cylinder *B*, of five litres capacity, could be filled with gas. After valve 1 was closed and valve 3 was opened, the pressure of the gas could be raised to the desired value by means of the hydraulic pump shown. The pump was

fed with a 50% glycerine-water mixture. The pressure bottles *D* and *E* contained calcium chloride and activated coconut charcoal respectively. The tube *F* contained copper oxide heated to 320° C. and the pressure bottles *G* and *H* contained solid sodium hydroxide and calcium chloride. The five

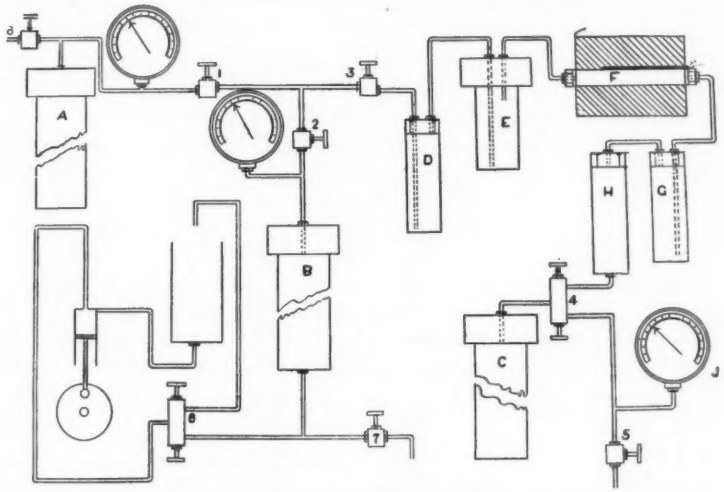

FIG. 1. *High pressure storage, compression, and purification apparatus*

litre vessel *C* acted as a subsidiary storage for gas at the pressure obtaining in the equilibrium pipette. Provision was made for heating this cylinder, and thereby raising the gas pressure above that possible by use of the hydraulic cylinder. Connection was made through valves 4 and 5 to the equilibrium pipette as desired. The pressure gauge, *J*, was used to determine the pressure of gas in the equilibrium pipette. This gauge, of standard Bourdon type construction, was calibrated frequently against a dead weight piston gauge certificated by the National Physical Laboratory, England.

The Equilibrium Pipette

A conventional drawing of the apparatus is shown in Fig. 2. It was so designed and assembled that the gas and liquid phases reached equilibrium with each other at a reasonable rate, and known volumes of each phase could be withdrawn for analysis.

The sample of gas phase was obtained from the upper, or gas phase, pipette, *A*, and the sample of liquid phase was obtained from the lower, liquid phase pipette, *B*. These pipettes were in communication from their ends with the two central reservoirs as shown, and could be isolated by closing valves 2, 3, 4, and 5. The materials in these sampling pipettes could be withdrawn through valves 6 and 7 and led through tube *E* to the analytical apparatus.

The volume of the sampling pipettes was determined by weighing the amount of mercury required to fill them under pressure. The volume of the

gas phase pipette was 11.206 ± 0.005 cc. and that of the liquid phase pipette was 21.002 ± 0.005 cc. The volume of each central reservoir was 60 cc. approximately. The pipettes were calibrated at intervals, and showed no appreciable change in volume.

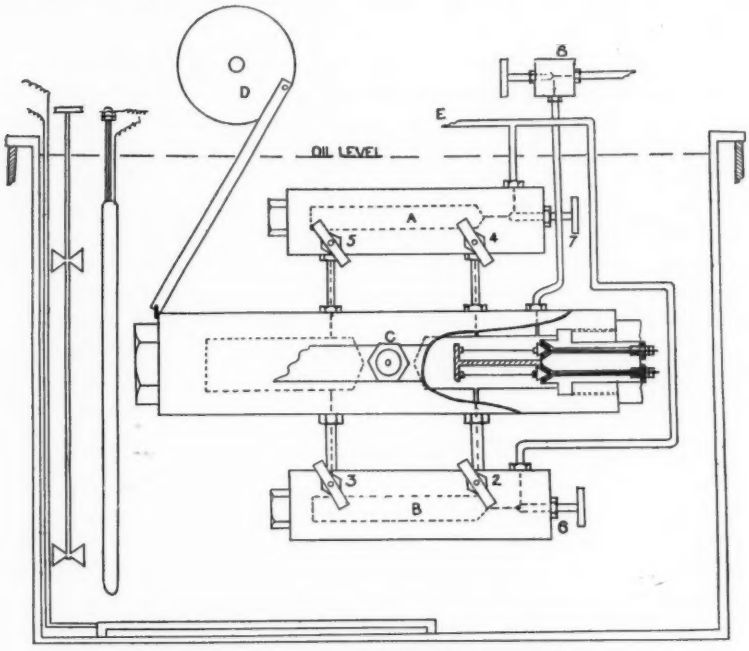

FIG. 2. *High pressure solubility pipettes assembly.*

The whole assembly was pivoted at *C* and could be oscillated through 90° by means of a gear train and crank, *D*. The gear train was so equipped with cams and a clutch that the pipette assembly was held in each extreme tilted position for one-half minute during each oscillation. The tilting motion was sufficiently rapid to provide agitation of the contents of the central reservoirs. Holding the assembly in each extreme position for one-half minute permitted the flow of liquid from the higher central reservoir through the liquid phase pipette to the lower central reservoir, the gas phase moving at the same time through the upper pipette. At high pressures near the critical value when the density difference between phases was small, it was necessary to assist the flow of liquid and gas. A close-fitting steel piston, which fell by gravity from one end of the pipette to the other as the assembly oscillated, was placed in the lower pipette. Leakage past this piston, while not great, permitted sufficient circulation to ensure uniform composition throughout the liquid phase.

The approximate liquid level in the central reservoirs when horizontal was ascertained by means of the electrical indicator shown in the cut-away section in Fig. 2. The indicator depended for its operation on the different thermal

conductivities of the liquid and gas phases. Two identical platinum wires, 2 in. long, 0.0015 in. in diameter, within the reservoir served as two arms of a Wheatstone bridge. The leads, of heavy steel rods, from the external circuit were insulated and made gas tight by double compression cones of ebonite. A small constant current, 0.06 amp. was fed to the bridge and served to heat the wires slightly. A sensitive wall-type galvanometer served to indicate balance in the bridge. When the liquid level was between the platinum wires, the galvanometer showed a large deflection. If both wires were in the same phase, there was little or no deflection. Thus, the liquid level could be determined to within about $\frac{3}{8}$ in. of the central line through the reservoir, a determination sufficiently accurate for work with systems substantially two-component. It was necessary only to ensure that there was, at all times, two phases in the apparatus, and the boundary was in the central reservoir.

The temperature of the pipette assembly was maintained constant to within 0.1° C. by means of a thermostatically controlled oil bath shown. The bath was heated electrically and could easily be raised to a temperature of 125° C. The whole bath, heaters and thermostat included, was designed in such a manner that it could be lowered clear of the pipette assembly in order to permit manipulation of valves.

The Analytical Apparatus

The essential parts of the collecting and measuring apparatus for dealing with the expanded contents of the pipettes are shown in Fig. 3.

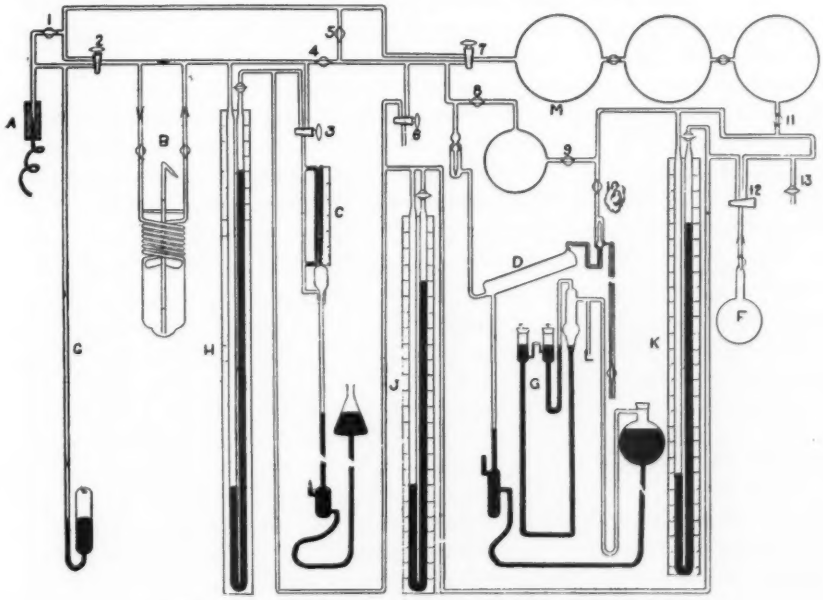

FIG. 3. *Expansion, separation, and measuring apparatus.*

Connection to the pipettes was made by means of a flexible copper tube ending in the glass-to-metal joint, *A*. A mercury sealed safety tube, *G*, protected the glass apparatus against accidental sudden liberation of the pipette contents. Pressures to the left of stopcock, *H*, were measured on manometer *H* or on the McLeod gauge *C*. A condenser, *B*, was attached, as shown, to the apparatus by ground glass joints, and could be removed for weighing. Other types of condensers, interchangeable with that shown, could be used when it was more convenient to do so. An automatic (7) Toepler pump, *D*, was used both as a circulating pump to mix the gases released from the pipettes, and to evacuate the pipettes; this ensured the removal of all the material in the pipette. The four bulbs, *M*, acted as a gas storage and measuring system in conjunction with the manometer *K*. The volume of each bulb was determined accurately, and the whole assembly surrounded by an air bath. No temperature control was used, the temperature in the bath being determined at the time of measurement by means of a calibrated thermometer within the bath. The volume of all tubing between stopcocks, 9, 10, 11, 13, and 12 was determined to a fixed high point on the left manometer arm. The volume of the manometer tube was also determined below this point. Three of the bulbs were of approximately two litres capacity, and the fourth, one litre. The volume of the tubing to the manometer was approximately 60 cc.

Samples of gas were taken through stopcock 12 to the half-litre bulb, *F*, of known volume for density determinations. The weight of bulb *F* was determined when evacuated and when full of gas in the usual manner, with a similar sealed bulb as counterpoise and calibrated weights. Samples of gas for combustion analysis were removed through stopcock 13.

Mercury diffusion pumps backed by an oil pump were connected to the apparatus through stopcock 6. These pumps were used in evacuation of the system prior to the releasing of the contents of the pipettes, and were used periodically to evacuate the right side of all manometers. The millimetre scales used with the manometers were calibrated periodically by comparison with a precision cathetometer.

Procedure

The pipette assembly, Fig. 2, was tested under pressure for leaks, evacuated, and flushed with gas from the storage system. A funnel was fitted to valve 8 and the correct amount of liquid, as found from experience, was added. With valves 6 and 7 closed, and valves 2, 3, 4, and 5 open, gas was admitted through valve 8 until the pressure was that desired. Valve 8 was closed, the oil bath raised into position, and oscillation of the assembly begun. After 15 min., connection was made to the gas supply, and the pressure adjusted to the desired value. This cycle of operation was repeated until no discernible pressure drop occurred in the pipettes after one hour of oscillation. The bath was lowered and valves 2, 3, 4, and 5 were closed. The contents of the sample pipettes were removed, the liquid sample first, through valves 6 and 7 in turn for analysis. In making a duplicate experiment, liquid to replace that

removed in the samples was introduced through *E* to the lower pipette, the appropriate valves adjusted and the procedure described above repeated. In this way the contents of the central reservoirs were not liberated.

The whole analytical apparatus, Fig. 3, up to the pipette connections, was evacuated. Stopcocks 1, 3, 5, 6, 7, 8, 12, 13, and 9 or 11, depending on the storage capacity desired, were closed, and 2 was opened to the pipette. A cooling mixture was placed around the condenser, *B*, and the valve on the pipette opened very slightly. The rate of expansion was such that about 100 cc. of gas per min. was liberated. When the pressure in the pipette had reached that of the analytical apparatus, the volume to the left of stopcock 7 was evacuated by means of the pump, *D*, to a pressure of about 4 mm. of mercury. The condenser was isolated and evacuation continued, with stopcocks 1 and 5 open, to a pressure less than 0.1 mm. of mercury. After stopcocks 1, 2, 4, and 5 were closed, the condenser was removed and weighed in order to obtain the weight of liquid recovered.

The gas, now in the bulbs, *M*, and the Toepler pump, was circulated for one-half hour or more by means of the pump until the composition was uniform. Stopcock 7 or 8, as the case might be, was closed, and the gas remaining back of the Toepler pump was passed into the bulbs, and the mercury level raised to stopcock 10, which was then closed. The pressure and temperature of the gas were measured, and density determinations made with the calibrated bulb, *F*. The volume of gas was calculated to N.T.P.

Samples of gas were passed through stopcock 13 to the combustion analysis apparatus. The gas always contained some small amount of the liquid hydrocarbon as vapor, and the amount was determined by combustion analysis, using a modification of the method of ultimate organic analysis for carbon and hydrogen (2). Combustion in the usual types of Orsat apparatus for gas analysis was not sufficiently precise to give the data required.

The data obtained as described above were sufficient to give the mass and composition of the contents of each sample pipette when the gas used contained only methane and nitrogen. The errors possible in the procedure were numerous but generally small. The pressures in the equilibrium pipette were reproducible to less than 10 lb. per sq. in., and the temperature was always constant to better than 0.1° C. The volume of the pipettes was known to about 0.04%, a variation that was negligible. The change in volume of the sample pipettes with pressure was calculated roughly to be 0.05% for the extreme range. Attempts were made to measure this change directly by filling the pipettes with mercury under different pressures. The change in volume with pressure as measured was less than the experimental error of 0.005 cc. Changing temperature had an appreciable effect on pipette volume. The increase in volume was calculated in every case and added to the volume found at 25° C. as a correction at higher temperatures.

The possibility of adsorption on the steel surface was eliminated by measurements of the volume of gas liberated at different pressures and with different areas of steel surface.

Errors in the method of analysis were relatively great and might reach 0.5% at the lower pressures used. At pressures greater than 1000 lb. per sq. in., however, this error was only one or two tenths of one per cent.

The chief errors appeared to arise in the equilibrium pipettes themselves. With a gas of two components, duplication of an experiment would require exactly the same amount of liquid and gas in the pipettes. This was only roughly true in this case. The increasing deviation between the results of experiments at the lower pressures may be attributed to the increasing relative error in pressure measurements. It did not appear possible to duplicate the conditions of equilibrium to better than 0.5% at the lower pressures or to about 0.2% at the higher pressures. Deviations between duplicates at the lower pressures reached, occasionally, 2%, particularly if a gas containing some ethane was used.

After the technique of operation had been systematized, it was possible to carry out an experiment in one day. A duplicate experiment required a second day and the calculations most of a third day.

References

1. BEECHER, C. E. and PARKHURST, I. P. Amer. Inst. Mining Met. Engrs., Pet. Div., 51. 1936.
2. BOOMER, E. H. and JOHNSON, C. A. Can. J. Research, B, 15 : 363-366. 1937.
3. BOOMER, E. H., JOHNSON, C. A. and THOMAS, V. Can. J. Research, B, 15 : 360-362. 1937.
4. DOW, D. B. and CALKIN, L. P. U.S. Bur. Mines, Rept. of Invest. 2732.
5. FROLICH, P. K., TAUCH, E. J., HOGAN, J. J. and PEER, A. A. Ind. Eng. Chem. 23 : 548-550. 1931.
6. LINDSLY, B. E. Trans. Amer. Inst. Mining Met. Engrs., Pet. Div. 252-274. 1931.
7. MAASS, O. J. Am. Chem. Soc. 41 : 53-59. 1919.
8. MILLS, R. V. A. and HEITHECKER, R. E. U.S. Bur. Mines, Rept. of Invest. 2893.
9. SAGE, B. H. and LACEY, W. N. Ind. Eng. Chem. 26 : 103-106. 1934.

THE OXIDATION OF METHANE AT HIGH PRESSURES

I. PRELIMINARY EXPERIMENTS[1]

By E. H. Boomer[2] and J. W. Broughton[3]

Abstract

Mixtures of oxygen and methane at pressures from 100 to 180 atm. were passed at various temperatures between 300° and 350° C. over some catalysts. Simple apparatus was used and analytical technique developed. The production of methanol as an important product of oxidation, together with small quantities of formaldehyde and formic acid, was shown. Yields of these three products as high as 37% of the carbon oxidized were obtained.

Introduction

Oxidation is one of the most common and certainly, from the practical point of view, the most important of the few general reactions of paraffin hydrocarbons. Reaction with oxygen may be brought about under various conditions of temperature, pressure, concentration, and with catalysts. Because the reaction is general and is of scientific as well as great practical interest, it has been the subject of much study. The significance of such another study lies in its practical applications rather more than in its scientific importance. The Province of Alberta is heavily endowed with supplies of natural gas of which the major component is methane. The possible daily production is several times greater than the demand and a great deal of wastage occurs. Some process yielding useful liquid products from the surplus gas is, obviously, of interest.

The direct production of alcohols, aldehydes, or even acids by oxidation of paraffin hydrocarbons is a process offering obvious attractions. In the case of methane, two stages are necessary, at present, for the production of methanol; these involve conversion to carbon monoxide and hydrogen followed by a catalytic reaction under pressure. The problem has received considerable attention in the past, particularly at pressures near one atmosphere. It has been shown conclusively by Bone and collaborators (4), by Wheeler and Blair (15), and others, that oxygenated derivatives were formed in the reaction of oxygen with paraffin hydrocarbons at low pressures. The yields of alcohol, aldehyde, or acid were, however, very small. More recently, claims have been made (3, 9) of higher yields by the use of nitrogen oxides as gaseous catalysts. Another report of high yields at low temperatures and pressures with solid catalysts has also appeared (6). From a study of the results reported and much unsuccessful work here, the writers have been convinced that yields of useful products of practical interest cannot be obtained at low

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Contribution from the Chemical Laboratories of the University of Alberta, Edmonton, Canada, with financial assistance from the Research Council of Alberta and the National Research Council of Canada.
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pressures. Consequently, attention was turned to the use of pressure as a means of improving yields and suppressing undesirable reactions in the oxidation of methane.

The application of the "hydroxylation" theory proposed by Bone (4) to the process suggests clearly that an increase in pressure would result in more methanol and less of the succeeding products of oxidation. This has been confirmed amply by Newitt and Haffner (11), Pichler and Reder (14), by Newitt and Szego (12), and by Yoshikawa (17), as well as in the work carried out in these laboratories. The use of the "peroxide" theory (5, 7) does not appear to be necessary in considering the oxidation of methane. Norrish (13) offers an alternative to the "hydroxylation" theory and suggests the production of free radicals as the primary step followed by that of formaldehyde as the primary stable product. The usefulness of the theories of Bone and of Norrish in the present work may be taken as evidence of their essential correctness.

On the practical side, the work of Wiezevitch and Frolich (16) only need be considered. They oxidized, under pressure, various natural gases with oxygen, in contact with various catalysts, and determined optimum conditions for the production of useful products. They showed that yields were high only if the concentration of oxygen was low, and the yield of useful products on the basis of carbon input per pass was low. This paper includes an excellent bibliography on the subject.

Much of the published results of work at high pressures appeared after the inception of the work here and, it may be said, confirmed substantially the authors' findings. The work to be described in this and succeeding papers deals primarily with methane, but includes, as in the present report, work on a gas containing small amounts of ethane and propane. The production of methanol in high yields and with large conversion per pass of reactants was desired. This paper will discuss generally some preliminary work and give details of a few experiments in which copper and silver were used as catalysts.

Experimental

A number of experiments were performed in which a large steel reaction vessel was used. The reactor was used empty and also with a variety of oxide catalysts at temperatures ranging from 235° to 450° C. and pressures of about 200 atm. Natural gas alone was employed in some experiments to determine whether the oxides were reduced by the hydrocarbons under the conditions of temperature and pressure used. A second series of experiments employed oxygen-natural gas mixtures containing 7.3% of oxygen by volume. No appreciable yields of useful products were obtained in any case. The oxide catalysts, including barium peroxide, vanadium pentoxide, and blue tungstic oxide were relatively inactive. Two Hopcalite type (10) catalysts were prepared and used. They promoted oxidation violently for a short time and then became inactive. An interesting result was obtained with the empty steel reactor. Oxidation proceeded rapidly and to completion,

and gave carbon oxides and water. The steel surfaces were corroded severely and much iron oxide was formed. The steel was a high nickel-chromium variety and when used as catalyst in the form of turnings showed no corrosion.

The lowest temperatures at which oxidation became apparent varied with the catalysts. The Hopcalite catalysts promoted oxidation at temperatures as low as 125° C. but after the initial action was over, a temperature of 310° C. was required. Silver promoted initial oxidation at 200° C. and required a temperature of 300° C. or higher for rapid reaction. Copper, steel, and the other catalysts showed activity at 250° C. Copper promoted rapid reaction at 325° to 350° C. and the others required temperatures in excess of 375° C. Copper and silver were found to be superior to all other catalysts in the promotion of desirable reactions giving methanol.

Following this preliminary work, a tubular, copper-lined reactor was built and a series of experiments were carried out using metallic copper and silver as catalysts with oxygen-natural gas mixtures containing 7.3 to 7.5% of oxygen. This series of experiments was of interest and provided experience upon which later work was based. The results will be presented, in part, in what follows.

Materials

Viking natural gas was used in all experiments. This is a dry gas of high methane content and of the following composition: methane, 95.7; ethane, 1.4; propane, 0.9; nitrogen 2.0%. The gas contained organic sulphur compounds which were introduced as an odorant before distribution to consumers. These sulphur compounds were removed in a manner that will be described in connection with the apparatus. The oxygen employed was the commercial gas obtained from liquid air and compressed in steel cylinders.

Mixtures of the natural gas and oxygen were prepared by passing the two gases through meters simultaneously and in the desired proportions to a water-sealed gas holder. The mixture was dried over calcium chloride and compressed into a steel storage vessel. Oxygen concentrations higher than 7.5% were not used because of the danger of explosions.

The copper wall of the reactor was used as one of the two catalysts. The other catalyst, silver on asbestos fibre, was prepared by reduction of silver nitrate with concentrated formic acid in the presence of acid-washed, long-fibre asbestos. The silvered asbestos was washed and dried.

Apparatus

The apparatus is shown in conventional form in Fig. 1. The gas mixture entered the apparatus through valve *A*, and passed through 98% sulphuric acid in the scrubber, *B*, which was filled with broken glass. The sulphuric acid completely destroyed the organic sulphur compounds, probably by oxidation (2), and the sulphur was converted to sulphur dioxide. The steel bottle *C* contained solid potassium hydroxide, which removed the sulphur dioxide and water. In bottle *D* activated coconut charcoal served to give the gas mixture a final purification. A recording Bourdon type gauge, *E*, gave

a record of the pressure throughout a run. The reaction tube, *F*, was placed vertically in the furnace, *H*. A heavy copper lining, *G*, between the furnace heaters and reactor served to aid in uniform temperature distribution. The volume of the reaction space in the reaction tube was approximately 7.5 cc. Temperatures were recorded and controlled automatically by means of an

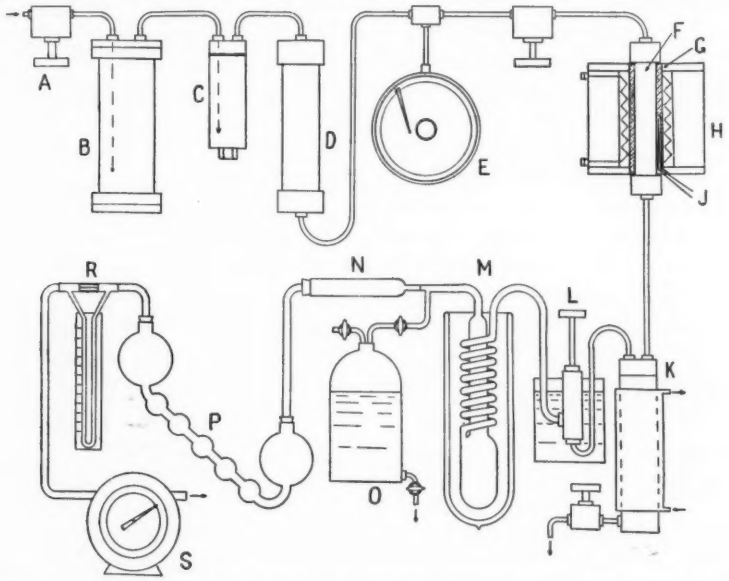

FIG. 1. *High pressure purification and reaction apparatus with low pressure recovery apparatus.*

automatic potentiometer and the thermocouple, *J*. Liquid products of the reaction were collected in the water-cooled high pressure condenser, *K*. In order to reduce corrosion, this condenser was chromium plated on the inside, and the connections to the reactor and expansion valve, *L*, were of heavy walled copper tube. The expansion valve, *L*, was capable of fine control of the gas flow and was maintained at a temperature of 100° C. by means of an oil bath. The expanded gas passed through the glass condenser, *M*, which was cooled in an ice-bath, then through a calcium chloride tube, *N*, to collect water vapor, and the water scrubber, *P*, to collect traces of formaldehyde that escaped condensation. A constant rate gas sampler, *O*, was used to take a continuous proportional sample of the off-gas. The rate of gas flow was shown by the flowmeter, *R*, and the quantity of off-gas measured with a test meter, *S*.

Analytical Methods

The liquid products in the high pressure condenser were blown into the ice-cooled glass condenser at the end of a run, and the weight was determined. The gain in weight of the calcium chloride tube was also determined. The

liquid products, together with the contents of the water scrubber, were made up to 100 cc. in a volumetric flask and measured portions were taken for analysis. The only method suitable for methyl alcohol determination was found to be that of Fischer and Schmidt (8). The method depends on the quantitative formation of methyl nitrite and its subsequent hydrolysis to methanol and nitrous acid by hydrochloric acid in the presence of potassium iodide. The liberated iodine is titrated with sodium thiosulphate. The method, with slight modifications in procedure, was found very satisfactory and precise. Certain identification of the alcohol present was obtained by preparation of the 3,5-dinitrobenzoic acid ester derivative, m.p. 106.8° C. A mixed melting point determination carried out with a laboratory reagent product and the ester prepared from the condensate gave the same value. Ethyl alcohol was also present in very small amounts as shown by the iodoform reaction. The ethyl alcohol may be attributed to the presence of ethane in the gas.

Formaldehyde was determined by Romijn's cyanide method using a modification of the procedure (1, p. 261) capable of high accuracy. Volhard's method of cyanide determination was used.

Formic acid was determined by warming a sample of condensate to drive off carbon dioxide, adding an excess of standard sodium hydroxide to decompose any salts or esters present, and back-titrating with standard acid. Copper salts were frequently present and copper hydroxide was precipitated with excess alkali. This was filtered off before back-titration with acid.

The gain in weight of the calcium chloride tube was taken as water. Analyses carried out on the contents of the calcium chloride tube showed less than 0.5% of the total methanol as having escaped the condensers. This quantity was within the experimental error in the procedure. Confirmation of the quantity of alcohol in the condensate was obtained frequently by fractional distillation in a vacuum jacketed column.

The analysis of both in-gas and off-gas was carried out with an improved Bureau of Mines Orsat apparatus. No measurement of the volume of in-gas was possible, but calculations based on the amount and composition of the off-gas and liquid products could be made. Carbon was used as the reference element in the calculation of material balances. Oxygen was not satisfactory because of an unexplained loss in most runs. This loss of oxygen will be referred to again.

Results and Discussion

The results of a number of runs with the copper lining of the reaction tube as catalyst and for two runs with silver catalyst filling the reaction tube are given in Table I. A considerable number of data have been omitted from the table, the principal figures being those giving the ratio of the volume of in-gas to off-gas. This figure was remarkably constant at 1.10, within the limits of error, in experiments in which the oxygen was all, or nearly all consumed. This is, of course, what might be expected; variations do occur but they are small. The ratio of the amount of oxygen passed in to that

TABLE I

THE OXIDATION OF NATURAL GAS UNDER VARIED CONDITIONS OF TEMPERATURE, PRESSURE, AND RATE OF FLOW

Experiment No.	24	26	27	28	29	30	34	45	46
Catalyst	Cu	Cu	Cu	Cu	Cu	Cu	Cu	Ag	Ag
Temp., °C.	325	325	325	350	350	350	350	310	312
Pressure, atm.	183	161	119	117	109	95	117	173	153
Off-gas flow, litres per min.	0.80	0.58	0.9	0.9	2.0	2.0	0.9	2.0	3.82
In-gas, oxygen, % by volume	7.3	7.3	7.3	7.3	7.3	7.3	7.3	7.5	7.5
Off-gas, % by volume									
CO_2	2.3	2.9	1.4	2.6	2.0	2.5	2.3	1.4	1.7
O_2	1.4	1.7	3.4	0.5	0.4	0.1	0.6	0.1	1.0
H_2	0.4	0.3	0.3	0·5	0·5	0·4	0·4	0·4	0·5
CO	0·6	0·8	0·7	1.4	1.9	2.0	1.5	1.6	2.3
CH_4	84.8	88.6	86.8	89.5	88.1	86.8	—	89.1	90.1
C_2H_6	2.4	0.0	0.0	0.0	0.5	1.4	—	0.0	0.0
% of total carbon oxidized	4.40	4.95	2.93	5.65	5.94	6.30	5.88	4.40	4.85
Yields, as % of carbon oxidized to,									
Methanol	35.9	25.3	27.1	30.2	34.2	29.7	31.8	31.5	17.9
Formaldehyde	0.8	1.0	1.0	1.2	0.9	1.7	2.1	1.7	1.4
Formic acid	0.0	0.0	0.0	0.4	0.3	0.1	3.2	0.6	0.4
Total	36.7	26.3	28.1	31.8	35.4	31.5	37.1	33.8	19.7
Concentration of methanol in condensate, wt. %	38.7	31.2	36.2	33.0	36.7	40.6	33.8	24.4	19.8

emerging, as found in all products has been omitted. This ratio was less than 1, generally, and varied erratically. The loss of oxygen has not been accounted for, and in later work, to be published, definite attempts were made to find the source of the discrepancy. The phenomenon is not new and has been reported elsewhere (16), also without explanation.

From 5 to more than 10 cu. ft. of gas, measured at N.T.P., was used in each experiment and the weight of condensate varied between 2 and 3 gm. per cu. ft.

While many duplicate experiments were made, only one pair has been included in the results given. Experiments Nos. 28 and 34 were selected as being typical duplicates. It will be seen on inspection that the results are substantially the same in each case, excepting only in formic acid production. The variations shown were usually found with duplicate runs and have been attributed to temperature changes. The reactions are highly exothermic and precise temperature control was impossible, even though automatic control was supplemented by manual control. Variations of as much as 10° C. from the temperatures tabled existed occasionally for a few minutes in most runs.

The runs given in Table I are sufficient to show, at least qualitatively, the effect of the several variables on yields. Considering Nos. 27 and 28, carried

out at substantially the same pressures and rates of flow, it is evident that the yield of useful products has been more than doubled by a 25° C. rise in temperature. At the rate of flow used, little more than half of the oxygen was used at 325° C. This accounts for the low consumption of carbon. The efficiency of the process measured by the fraction of carbon oxidized and entering into the formation of useful products was slightly greater at the higher temperature. With temperatures lower than 325° C. reaction was very slow and methanol production small. At higher temperatures, above 350° C., oxidation proceeded very rapidly, and the methanol yield fell off above 375° C. even at high rates of flow.

The effect of pressure is generally evident at both temperatures when the different rates of flow are taken into account. From a comparison of Nos. 24 and 27, it is seen that a decrease in pressure results in lower carbon consumption and a lower efficiency in the conversion of carbon to compounds. The change is too great to be attributed to the slight increase in rate of gas flow. From a consideration of No. 26, together with the other experiments, the effect of rate of flow is evident. The reduced rate of flow resulted in a greater carbon consumption, but the efficiency of production of compounds was decreased greatly. The efficiency is very much less than that found at the higher pressure and rate in No. 24, but is also less than that found at a lower pressure and higher rate of flow shown in No. 27.

Generally, a study of both series of experiments shows the effect of changing pressures and rates of flow. Within the limits used, increasing pressure gives greater carbon consumption and higher conversion to compounds. The effect of changing rate of flow appears to be more complicated. At low rates, carbon consumption is high, but the conversion to useful products is low because of more complete oxidation resulting in formation of carbon oxides and water. As the rate of flow is increased, other things being equal, carbon consumption is decreased, but the efficiency of conversion to compounds increased. Obviously, with the practical criterion, conversion of total carbon to useful compounds, as a measure, there is an optimum rate of flow at which the two opposing factors give a maximum production of methanol. For the present apparatus, at 100 atm. and 350° C., it would appear that the optimum rate of flow is at least two litres per minute measured as off-gas.

The results with the silver catalyst, Nos. 45 and 46, are interesting, particularly in showing the greater activity of silver in causing rapid reaction at low temperatures. The decreased production of methanol in spite of a higher consumption of carbon in the second experiment is unexpected. More of the carbon appeared as carbon oxides, particularly carbon monoxide. This would suggest that the equilibrium between methanol and its decompsoition products, carbon monoxide and hydrogen, plays a part in the process occurring in the reaction tube. Alternatively, it should be pointed out that the reaction temperature may have been very much higher in the second experiment because of the poor heat conductivity of the catalyst.

While the silver catalyst cannot be compared, except roughly, with the copper catalyst because of differences in physical form, it is of interest to discuss their different actions. The copper catalyst always contained oxygen, probably in the form of cuprous oxide. Starting with a fresh pure copper surface, reaction resulted in pitting and a change in color to that of cuprous oxide. On the other hand, the silver catalyst was reduced and did not show any traces of silver oxide. That silver differed from copper in its actions was also shown by the production of methyl formate. Over copper, only traces of the ester were ever found while with silver, most of the formic acid appeared as methyl formate. This result may of course be attributed to the asbestos support used, a more probable catalyst for esterification. It should be pointed out finally that the temperature given, representing that of the reactor wall, may differ greatly from the temperature of the silver catalyst because of the poor heat conductivity of asbestos and the exothermic nature of the reactions.

It was expected that the higher hydrocarbons would be oxidized most easily and be absent from the off-gas. This was generally true, but exceptions occurred that could not be attributed to experimental error. Later work showed the possibility that higher hydrocarbons were synthesized in the process. The subject will receive further consideration in another report.

References

1. ALLEN'S COMMERCIAL ORGANIC ANALYSIS, Fourth Edition. P. Blakiston's Son and Co., Philadelphia. Vol. I. 1909.
2. BADNER, J. F. Thesis, University of Alberta. 1935.
3. BIBB, C. H. and LUCAS, H. J. Ind. Eng. Chem. 21 : 633-638. 1929.
4. BONE, W. A. Proc. Roy. Soc. (London), 134A : 243-274. 1932.
5. BRUNNER, M. and RIDEAL, E. K. J. Chem. Soc. 1162 - 1170. 1928.
6. CRISTESCU, J. Fuel, 1 : 23-25. 1935.
7. EGERTON, A. C. Nature, 121 : 10. 1928.
8. FISCHER, W. M. and SCHMIDT, A. Ber. 57 : 693-698. 1924.
9. LAYNG, T. E. and SOUKUP, R. Ind. Eng. Chem. 20 : 1052-1055. 1928.
10. MERRILL, D. R. and SCALIONE, C. C. J. Am. Chem. Soc. 43 : 1982-2002. 1921.
11. NEWITT, D. M. and HAFFNER, A. E. Proc. Roy. Soc. (London), 134A : 591-604. 1932.
12. NEWITT, D. M. and SZEGO, P. Proc. Roy. Soc. (London), 147A : 555-571. 1934.
13. NORRISH, R. G. W. Proc. Roy. Soc. (London), 150A : 36-57. 1935.
14. PICHLER, H. and REDER, R. Z. Angew. Chem. 46 : 161-165. 1933.
15. WHEELER, T. S. and BLAIR, E. W. J. Soc. Chem. Ind. 42 : 81-92 T. 1923.
16. WIEZEVITCH, P. J. and FROLICH, P. K. Ind. Eng. Chem. 26 : 267-276. 1934.
17. YOSHIKAWA, K. Bull. Inst. Phys. Chem. Res. (Japan), 10 : 305-315. 1931.

IMPROVED PACKED FRACTIONATING COLUMNS[1]

By D. F. Stedman[2]

Abstract

The factors limiting the utility of packings for fractionating columns are considered in detail. In view of these factors a type of packing is described which gives an effectiveness up to 20 plates per foot of height, and has a capacity at least equal to similar equipment of lower efficiency.

These packings are constructed of fine mesh wire gauze, and special constructions are described for laboratory use and also for high capacity apparatus.

The method of calibration is given and factors are evaluated for comparison of packings for batch and for continuous stills.

In work under consideration several years ago the need for a type of fractionating column of higher efficiency than types generally available was felt very seriously, and since preliminary experiments showed that very considerable improvement was possible, an attempt was made to find a really effective construction with the desired properties.

There are in general two types of column, the bubble tower and packed columns of various sorts. The former has proved very satisfactory for continuous fractionation, but for batch processes its large liquid tie-up is a decided disadvantage, while the packed type is of general utility. In this study it was also felt that such an enormous amount of work had been done on bubble plates under such a wide variety of direction, which had in fact achieved a very notable improvement, especially in capacity, over earliest types, and that further improvement along these lines was therefore improbable. In view of the fact that only minor changes had been found useful, despite very widespread commercial use and investigation, and that present plate efficiencies range from 50 to 85%, it would seem that this type of equipment is probably operating very close to its optimum. Further improvement must therefore come from some type of film contact, rather than from the dispersion of either phase in the other.

In a fractionating column the primary process of separation is the passage of constituents from the vapor through the interface to the liquid, and from the liquid through the same interface to the vapor. Now, in apparatus in general use for such fractionation, the relative velocity between the liquid and vapor at any particular point is quite small, a few feet per second. It is therefore evident that stagnant films of very appreciable thickness will be present on both sides of the interface, *i.e.*, there is a stagnant "boundary layer" of both liquid and vapor forming a partition at the interface through which the constituents must pass by diffusion processes. In any attempt to increase the effectiveness of fractionation apparatus, it is therefore of importance to consider the nature and speed of this diffusion process in order to make the best use of it.

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If k_m is the mean diffusion coefficient through the entire boundary layer of thickness S, and area A, and W the weight of ascending vapor, the change in composition which can be brought about in the vapor composition in unit time is

$$\frac{k_m A}{SW}\Delta X \ , \tag{1}$$

where ΔX is the deviation from equilibrium compositions from liquid to vapor.

In this expression k_m and W are fixed for any particular application, and, therefore, only A, S, and ΔX can be varied. Of these A can be varied directly but not without some correlation with other factors, such as liquid hold-up, while ΔX can vary only from 0 to the equivalent of one theoretical plate, and S can be controlled by indirect methods only.

Thus in the design of fractionating equipment of the liquid-vapor equilibrium type, only the following modifications can improve their efficiency:—

A. Increase in the contact area between liquid and vapor phases.

B. Increase in the time of contact of the two phases.

C. Improvement of the "natural mixing coefficient" of the body of liquid and vapor by so shaping the parts that the work available for the production of turbulence is utilized in the best manner.

D. Increase in column heights, so that more work may be available for production of turbulence in the liquid phase.

E. Increase in the back pressure on the column so that more work may be available for production of turbulence in the vapor.

F. Addition of mechanical work to increase turbulence, by means of moving elements.

G. Distribution of the available work between the two phases so that they are both mixed at "equivalent" speeds, and work is not wasted in mixing one phase too much and the other too little.

H. The design of the column so as to secure more even distribution of both liquid and vapor across the column section.

In general consideration of the utility and limitations of these methods of improvement, it is obvious that *A* directly increases the effectiveness, but it must be noted that such increase in the contact area is generally accompanied by an increase in the liquid tie-up, which if directly proportional is not beneficial in batch distillation.

In general *B* can be accomplished only by increasing the volume of the column which is not desirable. *C* is obviously advantageous, as far as it can be carried, but both *D* and *E* are definitely undesirable for many reasons, and in fact the main purpose of the present and similar work is to effect a reduction in these items.

Unless definitely beneficial results can be obtained by F which cannot be achieved otherwise, this seems to add a distinct complication to the apparatus, which if possible should be avoided. G is obviously desirable, but it is rather difficult to evaluate how far any particular construction deviates from the ideal in this respect, while H is entirely advantageous, but can be carried only to the point of uniformity.

Thus the items of design which can be examined to secure improvement, other than mechanical moving parts, are: (1) to obtain as large a contact area as possible, while keeping the liquid tie-up at a minimum; (ii) to shape the parts to obtain good mixing in both phases; (iii) to distribute the mixing between the phases to give equivalent and suitable mixing to both, and (iv) to design the column to secure even distribution of both phases across the column section.

After these items have received attention, the question of the use of added mechanical power to increase either the capacity or effectiveness of the column can be considered.

General Consideration of Factors Involved in Packed Columns

As turbulence, or bulk mixing, and diffusion, or molecular mixing, play such important roles in these phenomena, it is useful here to note the physical properties of the types of liquids and vapors concerned in the processes, and check over the general considerations involved in an attempt to find the factors limiting the effectiveness of present equipment.

Table I gives approximate values for the densities, diffusion constants, and viscosities, showing the range in which most liquids and vapors fall. Little work has been done on diffusion at elevated temperatures and consequently

TABLE I

AVERAGE VALUES FOR CERTAIN PROPERTIES OF LIQUIDS AND VAPORS

Density, D, of liquid at b.p.	0.5	1.5
Density, d, of vapor at b.p.	0.001	0.005
Diffusion constant of liquid, K, cm²/sec. at 20° C.	5×10^{-6}	2.5×10^{-6}
Diffusion constant of vapor, k, cm²/sec. at 20° C.	0.1	0.05
Viscosity of liquid at b.p.	0.002	0.004
Viscosity of vapor at b.p.	0.001	0.0002
$\sqrt{K/k \cdot D/d}$	3.5	2.1
$\sqrt{k/K}$	0.007	0.007

the values have been taken from data at 20° C. As no effort is made in this paper to obtain great accuracy in these calculations, these values will be adequate for present consideration if allowance is made in an approximate manner for the effect of higher temperatures.

Useful Film Thicknesses in Both Phases

Let F be the thickness of the boundary layer on the surface of the liquid, and f the thickness of the similar layer in the vapor; also let Δx be the change in composition from the interfacial liquid to the body of the liquid, and $\Delta' x$ the change in composition from the interfacial vapor to the body of vapor.

If the notation indicated in Table I is used, the weight of substance diffusing from the body of the liquid to the interface through area A in time t is

$$\frac{AtDK(\Delta x)}{F} ,$$

while the similar quantity for the vapor is

$$\frac{Atdk(\Delta' x)}{f} ,$$

which quantities are equal (on the assumption that the latent heats for the constituents being separated are equal).

Therefore,

$$\frac{F}{f} = \frac{DK(\Delta x)}{dk(\Delta' x)} . \tag{2}$$

Now the film in the vapor is set up by the material passing through the interface from the liquid, and conversely the film on the liquid side of the interface is formed from material from the vapor. Consequently, if a portion of vapor is suddenly placed in contact with liquid at the same temperature, but with which it is not in equilibrium, the amounts of the liquid and vapor constituents passing each way will be equal, and as a first approximation

$$DF(\Delta x) = df(\Delta' x) . \tag{3}$$

Owing to the shape of the diffusion waves set up this is not exactly correct, but is quite adequate for obtaining an insight into the fundamental factors involved.

Substitution of the value of x from Equation (3) in Equation (2) gives

$$\frac{F^2}{f^2} = \frac{K}{k} , \text{ or } \frac{F}{f} = \sqrt{\frac{K}{k}} \tag{4}$$

and the liquid film is therefore

$$\frac{FD}{fd} = \sqrt{\frac{K}{k}} \cdot \frac{D}{d} \tag{5}$$

times heavier than the vapor film.

The values of film thicknesses for the usual range of liquids and vapors have been calculated from Equations (4) and (5), and are given in Table I, from which it will be seen that the useful film of liquid weighs two to three times as much as the similar vapor film, and from the value of $\sqrt{k/K}$ is about 140 times thinner.

Flow Conditions, or Turbulence in the Vapor

It is also necessary to consider the state of turbulence of the phases, and as an example the turbulence conditions for vapor rising with a velocity of 30 cm. per sec. in tubes 1 cm. diam. might be calculated, using mean properties from Table I. Reynolds number (velocity × diameter × density ÷ viscosity) under these conditions is 500. As the critical value for a straight tube is 2000, such flow would be streamline. However, for conditions other than a straight smooth tube the critical value is lower, and for a circular tube with a single partition, provided with a central hole, faint turbulence is obtained at a Reynolds number of 250, and is very decided at 500. If further partitions across the main tube are added the first sign of turbulence naturally builds up as each partition is passed. However, as the flow pattern past such a partition is quite smooth and laminar at a Reynolds number of 200, it is to be expected that additional partitions would then have no effect. Such a tube, with many partitions, is evidently very similar to a very much bent path such as obtains in the vapor passages of a packed column.

From the above it is evident that with vapor velocities of 30 cm. per sec. in tortuous passages 4 mm. or less in diameter, streamline flow is obtained with most vapors at room temperature, and at higher temperatures even larger openings would still give laminar flow, as the density is decreased by heating and the viscosity increased.

The importance of turbulence in the vapor may be noted by the following simple calculation. Consider a column filled with 4 mm. tubes, and assume that no resistance is offered to diffusion by the liquid films, and calculate the amount of interchange by diffusion into the non-turbulent vapor stream, assumed to be rising at a rate of 30 cm. per sec. If a mean value for the diffusion constant be substituted in Equation (1), using an approximate path length of 2 mm., it will be seen that about 0.4 cc. of vapor will diffuse for each square centimetre of contact area per second. Since 30 cc. of vapor passes upwards per second, this gives a rate of doing fractionation work of 0.4/30 theoretical plates for each square centimetre of contact area per square centimetre of column section, or it would require 75 sq. cm. of contact area per square centimetre of column section to give one theoretical plate, if perfect distribution of both phases is assumed.

Now, short lengths of 4 mm. tubes, 4 mm. long, packed irregularly give 4.7 sq. cm. of contact area per cubic centimetre, so that such a column, with perfect distribution of both phases and streamline vapor flow would need 16 cm. per theoretical plate. Thus without turbulence even such fine packing as 4 mm. tubes, used under ideal conditions as to liquid distribution, which certainly cannot be realized in practice, gives hardly two plates per foot of height.

If, however, the flow were turbulent the concentration gradients at the interface would be much higher, and large increases in efficiency might be expected if the liquid could be distributed in such thin uniform films that the original assumption is approached.

Flow Conditions in the Liquid Phase

It is also desirable to consider the most suitable speeds at which the reflux liquid should be mixed in order to prevent the accumulation of products absorbed from the vapor in the surface of the liquid. Suppose the column contains n times as much liquid as vapor, any mutual transfer of material affects the liquid composition n times less than it does the vapor, and consequently mixing must take place n times more frequently in the liquid in order to change the composition of the bulk of liquid as rapidly as that of the vapor.

Now the minimum height in which the vapor must be mixed is one theoretical plate, so that if $n = 40$, a very common value, and it is hoped to achieve 10 theoretical plates per foot of height, the liquid must be mixed at least 400 times per foot, or the surface film, at least, must be "turned in" 33 times per inch of height to achieve this result, and if any lack of uniformity exists in the distribution of either phase, whereby efficiency will be lost, the liquid must be mixed even more rapidly.

Comparison of Existing Columns with the Above Requirements

In applying the above considerations to the usual types of packing it is evident that in most cases the turbulent conditions are reasonably well fulfilled in the vapor phase, although there is little doubt that with some laboratory packings made from very small objects the vapor flow is in the main streamline. However, the very frequent subdivision of the vapor stream is somewhat equivalent to turbulence and there is little doubt that many packings rely entirely on this effect.

With respect to rapidity and uniformity of mixing in the liquid phase, many packings evidently could be improved considerably, as quite large drops of liquid collect between parts of the packing and descend bodily in a random manner. There is also obviously room for improvement in many cases in the bulk distribution of both phases, *i.e.*, avoiding channeling; and also in the micro-distribution, *i.e.*, ensuring that every portion of liquid and vapor acts respectively in the same manner at the same speed throughout the column, and many packings could be improved very much in respect to the production of thin uniform liquid films, which are obviously desirable both for reducing liquid tie-up, and for obtaining good contact with the vapor.

Application of These Considerations to Actual Packing

In order to obtain as rapid and continuous mixing of the liquid as possible, it seemed that if the surface over which the liquid flowed were made very rough this might help the process. It was also desired to use an orderly arrangement rather than to rely on "the uniformity of complete disorder", and obtain as large an area of interface as possible with the least amount of liquid. As a material to satisfy all of these requirements, wire gauze seemed to offer interesting possibilities, which it was felt had not been explored at all completely.

Wire mesh has been used fairly extensively in fractionating columns, but experiments on such material as fly screen showed that although it may be built into a packing in a regular manner, it acts in an essentially random manner, *i.e.*, drops and streams of liquid collect and pass downwards in random positions governed by surface tension and the chance irregularities in the material while very little of the reflux is properly distributed. Tests on different meshes, however, showed that if quite fine gauze is used continuous films are produced and the process is quite different, in that the material floods all over and the flow of liquid can be definitely controlled by the shape of the structure over which it flows, without that extreme sensitivity to microscopic irregularities so noticeable with the coarser meshes.

It was found that about the most satisfactory mesh sizes were from 56 to 60 warp wires per inch and from 36 to 40 shute wires, using about 10 mil wire. It will be seen that the wire is quite heavy for the mesh, and is in fact as heavy as can be woven, in order to increase the roughness of the surface as much as possible. This size gives a capillary rise of 18 to 22 mm. with most organic solvents at room temperature if shaken with the solvent in a closed tube, and this effect evidently contributes considerably to the uniformity of flow of the liquid.

There now remains the question of the type of pattern to be used in forming packing from such material, and in this connection the latest and generally most satisfactory form will be described first, with the reasons for adopting it.

In Fig. 1 is shown diagrammatically a comparison between bad types of packing and good. Fig. 1, *A*, represents a vertical curtain of fairly coarse mesh, while Fig. 1, *B*, represents an edge view of an inverted V of fine mesh. The paths of liquid and vapor are indicated, and it will be seen that both diagrams are similar in this respect, with, however, the fundamental distinction that in *A* the liquid path is controlled entirely by chance irregularities and the flow of vapor, the liquid avoiding the vapor as much as possible; while in *B* the distribution of liquid is essentially independent of the vapor. At high vapor velocities the turbulence of the vapor will naturally disturb the smooth flow of the liquid, form ripples, etc., but on the average both limbs of the V will be equally affected. Thus *A* illustrates a cumulative effect, and if the structure is continuous complete segregation of both liquid and vapor will result, with a minimum of intermingling, while with *B* slight unavoidable irregularities will cause one side of the V to receive more liquid than the other, but as the vapor no longer controls this ratio the effect is not cumulative, and on the average a uniform and stable distribution of liquid is produced.

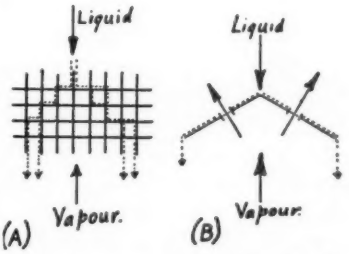

FIG. 1. *Comparison of bad (A) with good (B) types of liquid and vapor flow.*

Thus with the construction shown in Fig. 1, *B*, the primary subdivision of the liquid takes place at the apex of the V, and is, what might be termed, a structural subdivision, which is not affected either by the amount of vapor that happens to be passing upwards through this point in the packing, or by the fraction of this vapor that passes out of either side of the V. Conversely the above considerations also apply to the vapor flow, and this type of construction, therefore, removes the interaction of liquid and vapor and provides no mechanism by which channeling can be initiated.

In Fig. 2, *A*, is shown a plan and elevation of a single cellular element shaped to make use of the principle of Fig. 1, *B*. It will be seen that it is simply a cubical or rhomboidal box standing vertically on one corner. The lowest corner is truncated to provide an entrance for vapor, and exits are provided at the other three lowest corners. Thus liquid poured on to the apex of the cell will be divided into three streams, one on each face, and the rising vapor will be subdivided similarly, each process being independent of the motions of the other phase.

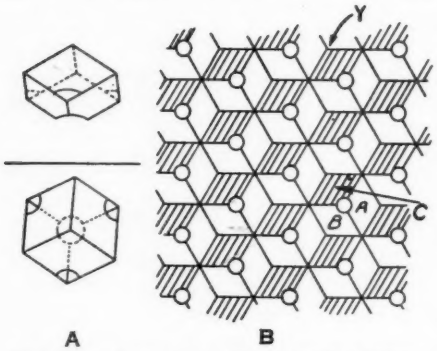

FIG. 2. *A. Single gauze cell. B. Sheet of gauze.*

Cells of this type might appear rather complex to use as column packing, but they are actually produced in a basically simple manner. Sheets of gauze are perforated with a series of equidistant holes, and are stamped into a pyramidal pattern. This pattern is indicated in Fig. 2, *B*, where the point *Y* is intended as a raised triangular pyramid, and each hole (henceforward to be referred to as *O*) is at the bottom of a pyramidal indentation. These sheets are then stacked together, the next sheet being placed in the same orientation above that indicated in the figure, but with a lateral shift, point *Y* being over point, *O*. The sheets are then spot-welded into position and the process repeated. This builds up a continuous lattice of cellular elements exactly similar to Fig. 2, *A*, the only difficulty being the fact that rather complex presses are required to produce the stamped sheets of gauze.

No diagram of the completed structure is given as it is almost impossible to make such a diagram in an illuminating manner, and the path taken by the liquid and vapor is perhaps best seen by considering the passage through each element. It will be seen that there is a cell directly beneath points *A*, *B*, and *C*, Fig. 2, *B*, and if the next sheet is added there will be a cell directly over *O*. Thus the opening *O* is fed with vapor equally from each of the cells under *A*, *B*, and *C*. and this vapor after passing through the cell above *O* is again divided into three streams as it passes upwards through the next layer of cells.

It will also be seen that each edge of each cell throughout the packing is a junction line for four plane surfaces of gauze, two of these planes supply liquid to the junction line, and, after the two films of liquid are partially mixed at the junction line, this liquid is redistributed over the two lower planes. It is therefore evident that with this constant mixing and redistribution of both phases no appreciable deviation from uniformity can exist, either in the amount passing through or the composition of either phase from point to point in any horizontal level in the column.

Mention might be made of the necessity of providing drainage at the bottom of this packing. It is self-evident that if the liquid is simply allowed to fall from the lowest points of the bottom sheet, the edges of the vapor holes, the hanging drops of liquid will lose all capillary effect and be blown about freely by the rising vapor. The capacity of the column will then be limited entirely by this effect, and will not be more than about half its normal value. This is prevented by attaching narrow depending strips of gauze about $\frac{5}{8}$ in. long, one for each vapor perforation, as shown in the lower part of Fig. 3. These maintain capillarity till the liquid is well below the vapor opening and allow the full capacity of the packing to be utilized. Other methods of drainage may also be used, but this is the method usually adopted for laboratory packings.

FIG. 3. *Conical pattern.*

This type of packing, termed the "hexagonal" pattern, has been made in sizes up to 6 in. diameter, and larger sizes are now under development, but for laboratory uses an even more effective type of packing has been developed. This is illustrated in Fig. 3, and consists of a series of gauze discs pressed into truncated cones and welded alternately base to base, and edge to edge. Each disc has a vapor perforation at one side as indicated by the dotted line, and the vapor, after passing through each cell by means of these openings, passes between the containing tube and the gauze round both sides of the axis before passing to the next cell.

It will be seen that the liquid is alternately brought together at the base of each cone and spread in a film over the broad portion of each surface, this action preventing variation in composition from point to point in the liquid. The vapor is also treated somewhat similarly in that it passes in a single turbulent stream through each cell, and then divides into two streams, passing behind and in front of the packing. In this case, mixing is somewhat less important, as each phase passes through the packing in practically one stream.

It will be seen that this type uses a rather longer path of contact than the "hexagonal" packing shown in Fig. 2; this gives it a greater height effectiveness, but at the same time decreases its capacity. These factors can be controlled quite readily by the depth of pressing, and the size of vapor opening,

but naturally capacity can be increased only at the expense of effectiveness, or *vice versa*. As at present made in 1 in. tubes the proportions are chosen to give 20 cc. of hexane per min. capacity at total reflux.

Calibration Procedure

Many attempts were made to calibrate columns two or three feet long, but this was ultimately abandoned as the results were often very misleading, and it has been found most satisfactory to calibrate quite short lengths, of not more than five theoretical plates. For this purpose a mixture of very highly purified *n*- and cyclo-hexanes is used containing about 25% of the former. A diagram of the column and stillhead arrangement is given in Fig. 4, and the procedure used is as follows:—

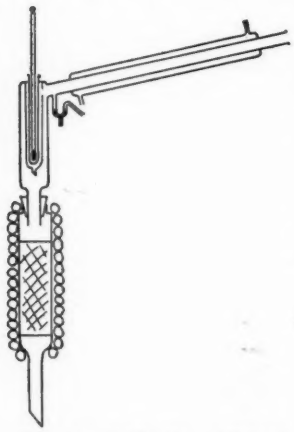

FIG. 4. *Calibration still-head.*

The boiler is electrically heated and the watts supplied measured, the heater wires being in contact with the flask as an aid in preventing "pumping". The whole flask and heater are buried in rock wool, while the column is wrapped in soft asbestos cord to keep heat losses uniform and small. The heat necessary to raise the vapor level just to the base of the packing is determined, and subtracted from the watts used in all experiments. As the columns are invariably quite small and the hexane very volatile, further insulation or actual heating of the column is not necessary. The vapor composition is calculated from the composition of liquid in the still (on the assumption of 1.2 theoretical plates of separation), and the latent heat of this vapor is taken by a weighted mean from 30,160 J for cyclohexane and 28,600 J per mol for *n*-hexane. Vapor velocities are then calculated from the watts used and this mean latent heat. This calculated vapor composition is however not used in the calculation of the effectiveness of the columns.

Temperatures were originally measured with a platinum resistance thermometer, but as this temperature determines only when the column has reached equilibrium, a standard time of 20 min. boiling has been adopted as this has been found quite adequate for these columns when used in this manner, and an ordinary thermometer is now used as a check on the general operation.

The condensed liquid passes over a small reservoir, 1 cc. volume, blocked by a mercury seal, and after equilibrium is established the mercury is lowered and raised again rapidly, the small sample being caught in a cooled tube to prevent vapor loss from the hot liquid.

As the concentration of *n*-hexane in the pot is quite appreciable, about 25% in 200 cc. of liquid, the composition of the liquid in the pot at any time is obtained from its original composition. This is possible as the tie-up of liquid in the column is very small and small corrections only are required.

Corrections are, therefore, made to the original composition for:

1. Vapor loss during the initial heating of the flask, using the volume of air exhausted and the condenser temperature, and on the assumption that four theoretical plates of separation were involved. This figure was obtained by means of thermometer readings, and as a result the loss is largely *n*-hexane, but is usually only about 0.3 cc.

2. Liquid in the column and condenser. This is measured with petroleum ether at room temperature, in order to simulate the surface tension effects obtaining during normal use of the apparatus with hot liquids. Thus the ether is added (through a long tipped burette) to nearly the bottom end of the water jacket through the condenser at a definite rate till it drips from the packing, and the volume used is noted. The process is repeated at different speeds.

3. Continuous loss to the atmosphere while running the still.

4. Loss of each sample during examination and while returning it to the still.

This seems rather a complicated procedure, but it obviates the handling of two lots of samples with a resulting greater loss of material, and expedites the actual calibration procedure, at the expense of a little calculation. All these corrections are, however, quite small; thus No. 2 involves only 3 to 4 cc. of liquid in the usual test, and the actual losses are even smaller. The total consequently affects the result very little.

The cyclohexane, which was purified by distillation of c.p. grade, has a freezing point apparently 0.17° higher than is reported for the Bureau des Etalons standard material. This freezing point was measured with a thermometer freshly calibrated by the Reichsanstalt, but as this sample was not compared directly with the standard material this freezing point is cited simply as showing that the cyclohexane was of satisfactory purity for this procedure. The *n*-hexane was the best sample obtained during tests on hexanes which will be described elsewhere, and contained a few hundredths of 1% of both methyl cyclopentane and 3-methyl pentane. Separation of these traces of impurities will be entirely negligible when such small quantities are used in columns only a few inches high.

The packing used was from 2 to 6 in. high and was adjusted so that the concentration of *n*-hexane did not become too near 100%, generally not over 80%, and the separation coefficient (α) taken as 1.433 as a mean over the range from 25% to 75% *n*-hexane. Ideal solutions are assumed and the equations solved mathematically, rather than graphically.

Analysis of samples is made by either refractive index or apparent boiling point, or both, and both procedures have been standardized by means of mixtures of the actual samples subsequently used in the still.

In Table II is given a typical set of results obtained during calibration of a short length of the hexagonal packing with $\frac{3}{8}$ in. cells, at one low speed, a fairly high speed, and the flooding limit. These measurements are taken at total reflux for a series of speeds covering the entire range possible for the particular packing.

TABLE II

CALIBRATION OF 2 IN. OF $\frac{3}{8}$ IN. HEXAGONAL PACKING (19 SHEETS OF GAUZE)

	A	B	C
Total watts supplied to still	49	256	290.5
Corrected mol. percentage of *n*-hexane in pot at time sample taken	29.4	28.3	27.9
Corrected mol. percentage of cyclohexane in pot at time sample taken	70.6	71.7	72.1
Mol. percentage *n*-hexane in product at total reflux	75.5	56.3	58.5
Mol. percentage cyclohexane in product at total reflux	24.5	43.7	41.5
Calcd. theoretical plates (assuming $\alpha = 1.433$, and ideal solutions)	5.61	3.32	3.62
Plates correction by calibration without column (interpolated from plot) at same watts	2.55	1.20	1.19
Plates in column	3.06	2.12	2.43
Theoretical plates per foot height	18.36	12.72	14.58
Cc. per minute at bottom of column	7.1	56.0	64.2
Cc. per minute at top of column	5.9	56.8	65.6

NOTE:—*Column cross section, 1.096 sq. in.*
Original mol. percentage of n-hexane in pot, 30.1%.
Original mol. percentage of cyclohexane in pot, 69.9%.
Watts required to raise vapor line to bottom of packing, 19.
Watts required to raise vapor line to top of packing, 26.

In some cases the packing is then removed from the column and the still and empty column recalibrated in order to determine the efficiency with no packing, but in all final measurements a dummy column is substituted which, while similar to the actual column, is shortened by the length originally occupied by the packing. This shortened and empty dummy then corrects for any "end effects", without including a length of empty column as is involved in the more approximate method of removing the packing. The results are then calculated to theoretical plates with and without the packed section of column, and the difference in plates per foot of height is plotted against the speed of reflux in cubic centimetres per minute per square inch of column section.

Effectiveness Obtained with These Packings

A series of results showing the calibration of various types of packing made from fine mesh gauze is plotted in Fig. 5. The patterns used in these packings are:—

(1) Horizontal prismatic cells, of $\frac{1}{4}$ in. square section; as these are not as effective they have not been described in detail.

(2) The same as (1) but using 0.18 in. square cells.

(3) Cones of 105° included angle and discs in 1 in. tube.

(4) "Hexagonal" pattern as in Fig. 2, $\frac{7}{16}$ in. cells indented to 30° slope.

(5) As (4), $\frac{3}{8}$ in. cells, indented to give cubical cells.

(6) As (5), $1\frac{1}{2}$ in. cells, $\frac{7}{16}$ in. perforations.

(7) As (5), $1\frac{1}{2}$ in. cells, $\frac{3}{16}$ in. perforations.

(8) Conical pattern of Fig. 3, in 1 in. diam. tube.

The short vertical line at the end of each curve indicates the limiting speed at the flooding point, although No. 1 was not taken as far as this point.

It will be seen that these columns all give higher effectiveness at lower vapor speeds. This is perhaps partly due to the longer time of contact, but is no doubt partly produced by the gauze surface itself. Thus at lower reflux speeds it is correspondingly "drier", and the roughness of the surface is therefore more effective. The liquid is also present in thinner films, and therefore reaches equilibrium more rapidly.

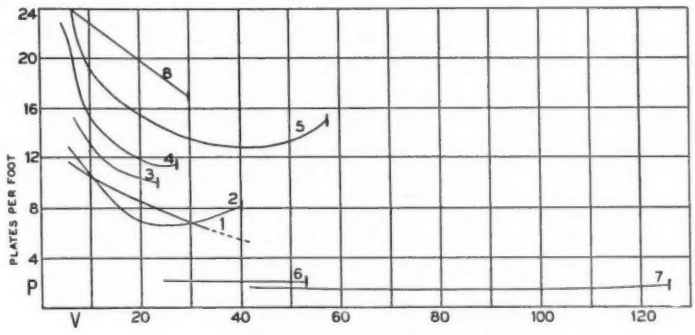

FIG. 5. *Plates per foot : reflux, cc./sq. in./min.*

This is in sharp contrast with the usual effect, which is either to show no change with speed, or in many cases a reduction of effectiveness at low vapor speeds. There is little doubt that the reduction often noted is due to the fact that channeling is taking place, and at low reflux speeds the liquid is not distributed properly, but passes downwards almost exclusively in the channeled streams. As channeling is not present in these columns, they are able to take advantage of the longer time of contact at slow speeds and thereby give considerably increased effectiveness.

Packings (1) and (2) give an interesting comparison, in that although (2) has 1.4 times the exposed surface of (1), it is actually less effective over a considerable range of speeds. This is evidently due to inadequate turbulence in the finer packing as these are of identical pattern except for the scale.

Packing (3) is somewhat similar to that shown in Fig. 3, but instead of pairs of cones, this pattern is made of truncated cones closed at the top with flat discs, two notches being cut in the edge of each disc for passage of vapor.

It will also be noted that Packing (8), Fig. 3, gives the greatest height effectiveness, but is limited in capacity while (5) gives the greatest effectiveness at fairly high speeds, and (7) gives the greatest capacity, at of course reduced height effectiveness. Packings (5) and (7) can be modified to give a continuous series of effects intermediate between these two curves, or even higher capacity can be secured by increasing the size of the pattern beyond the size of (7).

Liquid Tie-up in Gauze Packings

Another item of considerable importance in column operation is the liquid retained in the packing. Owing, however, to the very small amount retained by these columns it is a matter of some difficulty to make such a measurement while operating, and consequently the dynamic liquid tie-up has been measured for comparison purposes with benzene at room temperatures.

The values needed for correcting the composition of the mixture in the still during calibration were obtained by running petroleum ether (30° to 60° C.) through the column and measuring the volume retained. This is done in order to simulate the lower surface tension obtained at higher temperatures, but this procedure is not accurate enough for exact comparison. Benzene was therefore run through the packing at a definite speed for a few minutes, and the stream interrupted simultaneously at top and bottom and the whole weighed to give the amount of benzene retained.

Fig. 6 gives a plot of the results obtained with the same series of columns, expressed in grams of benzene retained per square inch of column section 1 ft. high.

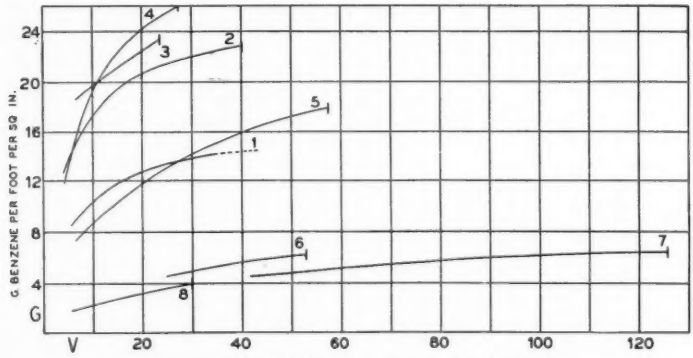

FIG. 6. *Liquid hold up: reflux, cc./sq. in./min.*

It will be noted that Packing (3) is bad in one respect, in that the liquid retained does not decrease much at reduced speeds. This is obviously due to the use of flat sheets, which do not drain well, as part of the construction. The fact that (4) is so much worse than (5) is due to a similar effect; although no flat sheets are used in (4), the angle of the packing was not steep enough to give as good drainage as (5). The other packings give values as might be expected in comparison with each other. (6), (7), and (8) are low owing to their open structure, while (5) is higher as it contains more gauze per unit volume.

It will be noted that these values are the dynamic hold-up for liquid at room temperature which differs appreciably from the amount retained when operating and heated. Thus examination of these packings in use in glass tubes shows that considerably less liquid than the plots indicate is retained over the lower speeds, corresponding to the falling portion of the curves in Fig. 5, while quite near the flooding point the amount increases rapidly.

Derived Factors for Evaluating Packings

In order to consider the utility of any packing it is necessary to combine the data of Figs. 5 and 6 in some manner, and consequently the following derived factors are introduced as indicating the specific utility of each packing for particular purposes. If the data of Fig. 5 is considered as values of $P : V$ and Fig. 6 as $G : V$, a value showing the specific utility of each packing for use in batch stills is obtained

$$\frac{G}{P} \times \frac{60}{V} = W ,$$

and W, therefore, gives the weight of benzene retained in a column of diameter such that it will reflux at 1 cc. per sec. and of one theoretical plate effectiveness, when operated at all values of V possible with that packing. W is therefore directly proportional to the amount of material represented in the cut-off between a standard pair of liquids when tested with each packing at the speed (V value) chosen, and should of course be as low as possible.

The values of W, plotted against V as before, are given in Fig. 7, and it will be seen that Packing (8) is very much the best at all speeds permissible, while (5) and (7) are best in the higher speeds.

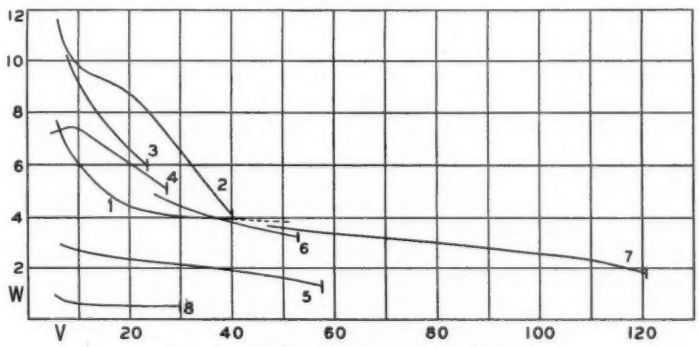

FIG. 7. *W factor : reflux, cc./sq. in./min.*

Another factor is of importance for comparison of packings for use in continuous stills. If the same notation is used,

$$\frac{V \times P}{60} = C$$

and it will be seen that C represents cubic centimetres per square inch per second $\times$ plates per foot, and is a volumetric capacity factor expressed in distillation work units, and should be as high as possible.

These values are given in Fig. 8, and it will be seen that Packings (8) and (5) are the best, and while (7) appears somewhat disappointing on this basis, it must be noted that this packing has hardly one-quarter as much gauze per cubic foot as the others, and is therefore much cheaper to make.

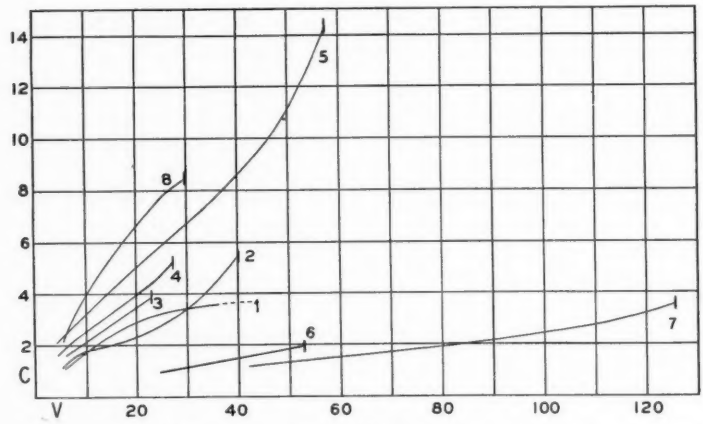

FIG. 8. *C factor : reflux, cc./sq. in./min.*

In order to permit comparison of the amount of work obtained per sheet of gauze, the *C* values of Fig. 8 were divided by the number of sheets of gauze per foot of height; this gave values for an economic factor *E*. These are plotted in Fig. 9, where it will be seen that on this basis (7) reaches values slightly higher than any other.

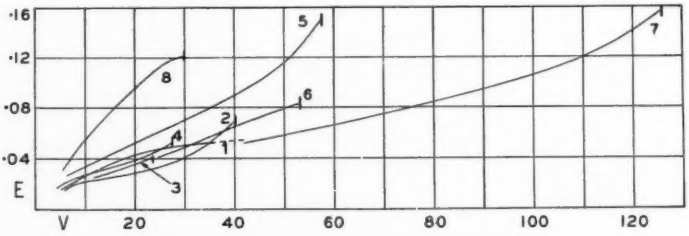

FIG. 9. *E factor : reflux, cc./sq. in./min.*

Comparison with Other Columns Available

In general, fractionating columns show a very wide range of properties corresponding to widely different classes of use, but Table III gives a rough comparison of about the range generally available, although this list is of course not intended as complete, but is simply a selection of the better known types. The values for the capacity and effectiveness of these columns are also calculated to the corresponding *W* and *C* values for comparison with the gauze packing, although it should be noted that the micro-laboratory type is not actually available in the capacity listed, as its sectional area is very small. They are all, however, compared on the same basis, of capacity per square inch.

It will be seen that the *W* values range from 0.48 for gauze packing (8) up to over 100, while Packing (8) is on this basis nearly four times better

TABLE III

COMPARISON OF VARIOUS COLUMNS

Type of column	Plates per foot, P	Liquid tie-up, G	Capacity, cc./sq.in./min., V	W	C
Small laboratory columns					
a. Micro-type	3	4	45	1.78	2.25
b. Indented tube type	1	5	40	7.5	0.67
c. Packed type	(to) 4	50	30	25	2.00
Commercial "fine chemical" columns	0.75	45	35	103	0.44
Crude oil columns	0.3	40	100	80	0.50
No. 8	16.7	4	30	0.48	8.32
No. 7	1.7	6.5	125	1.81	3.59
No. 5	14.9	17.9	57.5	1.25	14.3

than the micro type. It has also a much larger reflux capacity, and is very suitable for treating small volumes of liquid in much the same manner as a micro-fractionation.

Gauze packing (5), it will also be seen, has a very low W value, and is therefore very suitable for use in batch stills, while as it also has a very high C value, exceeding in this respect all others in the list, it is excellent for use in continuous stills.

Applications of Gauze Packings

The utility of Packing (8) for laboratory purposes of all sorts is obvious; it has a C factor much higher than is given by the usual packings, combined with the lowest W value, and while in this size it is limited to about 20 cc. of reflux per min. this capacity is adequate for many purposes. For purposes requiring a higher speed, Packing (5) gives very good results. This pattern has been made in sizes up to 3 in. diameter, in which size it will carry about 400 cc. of reflux per min. It also gives excellent height effectiveness and has a fairly low W value. For still higher capacities Packing (7) is the most suitable, it has a much lower height effectiveness, but for columns of large diameter this is not detrimental as it keeps the ratio of height to diameter at a reasonable figure, while the smaller patterns give such short lengths of packing that distribution of reflux over a large section becomes difficult. One of the main advantages of changing the size of the pattern is in fact to secure a column of suitable proportions.

One special use might also be noted for Packing (3), and any other pattern including horizontal sheets in its construction. These patterns are very useful for the treatment of mixtures which give two liquid phases, as the phase which does not wet the gauze is trapped on the horizontal surfaces, while patterns using only sloping elements allow this phase to "skate" over the continuous film formed by the other phase and pass downwards too rapidly for proper fractionation.

One further advantage of this type of construction* might also be noted, in that the actual weight of the packing is very small in comparison with such apparatus as bubble towers, etc., and consequently for use with corrosive materials a smaller quantity of the expensive alloys sometimes needed will produce a column of the required effectiveness and capacity. Thus in many cases, materials which may be prohibitive in cost if used in ordinary columns may be utilized in these gauze packings. For instance if Packing (7) is made of pure silver it would require 1 lb. of metal, per theoretical plate of effectiveness, per gallon per min. reflux; or a still equivalent to 20 theoretical plates for 10,000 gal. of reflux per day requires about 140 lbs. of silver in the gauze itself. At present prices this quantity of silver is worth about $750. The stainless steels are, of course, very suitable for many purposes, and in fact any alloy which can be drawn to wires may be used in these gauze packings for special purposes.

Experiments made with these packings and apparatus used with them will be described in later articles.

**Patents: U.S. 2,047,444, and in other principal countries.*